PB84-167584

Pilot Plant Tests of Chloride Ion Effects on Wet FGD (Flue Gas Desulfurization) System Performance

Acurex Corp., Research Triangle Park, NC

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Mar 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-167584

EPA-600/7-84-039
March 1984

PILOT PLANT TESTS
OF
CHLORIDE ION EFFECTS
ON
WET FGD SYSTEM PERFORMANCE

by

John C. S. Chang

Acurex Corporation
Southeast Regional Office
P. O. Box 13109
Research Triangle Park, NC 27709

EPA Contract 68-02-3648

EPA Project Officer: J. David Mobley
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

Prepared for:

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

pg. 23.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/7-84-039

2.

3. RECIPIENT'S ACCESSION NO.
PB84-167584

4. TITLE AND SUBTITLE
Pilot Plant Tests of Chloride Ion Effects on Wet FGD System Performance

5. REPORT DATE
March 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
John C.S. Chang

8. PERFORMING ORGANIZATION REPORT NO.
TR-83/1/SR

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Acurex Corporation
Southeast Regional Office
P.O. Box 13109
Research Triangle Park, North Carolina 27709

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-02-3648

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development*
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final; 9/81 - 9/83

14. SPONSORING AGENCY CODE
EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is J. David Mobley, Mail Drop 61, 919/541-2612. Cosponsored by Peabody Process Systems, Inc. (Job J-70020), Stamford, CT (Dennis Laslo, coordinator).

16. ABSTRACT The report gives test results from September 1981 through June 1983 of a chloride ion--Cl(-)--effects test program on a wet flue gas desulfurization (FGD) pilot plant, at EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC. Tests were conducted on a three-stage turbulent contact absorber (TCA) with 7.5 cu m/min (0.1 MW) flue gas capacity at Cl(-) concentrations of 160-180,000 ppm. The FGD processes investigated include conventional lime/limestone, magnesia enhanced limestone, organic dibasic acid (DBA) enhanced limestone, and limestone with two-tank forced oxidation. Data indicate that the effects of Cl(-) on the performance of the limestone scrubber are a function of cations associated with Cl(-) and scrubber operating conditions. The accumulation of CaCl2 caused decreased system pH and SO2 removal efficiency, occasional decreases of slurry settling rate, and increased gypsum scaling potential. Organic DBAs were found to be very effective in enhancing the SO2 mass transfer and counteracting the CaCl2 effects on SO2 removal efficiency. When magnesium was the cation, the increase of Cl(-) concentration improved SO2 removal efficiency when the Cl(-) concentration was below 40,000 ppm. No significant effects of NaCl were obtained at Cl(-) concentrations less than 50,000 ppm.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Calcium Oxides	Pollution Control	13B	
Chlorides	Magnesium Oxides	Stationary Sources	07B	
Desulfurization	Dibasic Organic Acids	Turbulent Contact Absorbers	07A, 07D	
Flue Gases			21B	07C
Coal			21D	
Calcium Carbonates				

18. DISTRIBUTION STATEMENT
Release to Public

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
21[illegible]

22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This report presents the test results from September 1981 through June 1983 of a chloride ion (Cl^-) effects test program on a wet flue gas desulfurization (FGD) pilot plant. The test facility is located at EPA's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. Tests were conducted on a three stage turbulent contact absorber with 7.5 m^3/min (0.1 MW) flue gas capacity at Cl^- concentrations ranging from 160 to 180,000 ppm. The FGD processes investigated include conventional lime/limestone, magnesia enhanced limestone and Organic Dibasic Acid (DBA) enhanced limestone.

Data indicate that the effects of Cl^- on performance of the limestone scrubber are a function of cations associated with Cl^- and scrubber operating conditions. The accumulation of calcium chloride caused decreased system pH and SO_2 removal efficiency, occasional decreases of slurry settling rate, and increased gypsum scaling potential. Organic dibasic acids were found to be very effective in enhancing the SO_2 mass transfer and counteracting the calcium chloride effects on SO_2 removal efficiency. When magnesium was the cation, the increase of Cl^- concentration improved SO_2 removal efficiency when the Cl^- concentration was below 40,000 ppm. No significant effects of sodium chloride were obtained at Cl^- concentrations less than 50,000 ppm. However, when Cl^- concentrations were greater than 70,000 ppm, both SO_2 removal efficiency and system pH decreased with the accumulation of either magnesium or sodium chloride.

The effects of calcium chloride on the performance of the lime scrubber were evaluated for both high and low sulfur coal cases. Significant effects on SO_2 removal efficiency and system pH were observed for high sulfur coal cases. No significant changes in SO_2 removal efficiency were obtained for low sulfur coal cases.

The accumulation of calcium chloride affected the performance of the magnesia enhanced limestone scrubber by reducing both SO_3^{2-} and $MgSO_3$ concentrations through chemical equilibrium effects. Pilot plant data indicated that the the decreases of SO_3^{2-} and $MgSO_3$ concentrations caused significant drops of SO_2 removal efficiencies.

The effects of calcium chloride on the performance of the DBA enhanced limestone scrubber were evaluated by both short- and long-term pilot plant tests. With the accumulation of calcium chloride, higher DBA concentrations were required to maintain constant SO_2 removal efficiencies. No effects of Cl^-on DBA degradation rate were observed. However, DBA coprecipitation rate increased at high calcium chloride concentration.

Pilot plant results indicated that oxidized product with greater than 96% gypsum and less than 2% calcium carbonate could be produced from the DBA enhanced limestone scrubber at high calcium chloride concentrations. With five displacements of wash water and three stage countercurrent washing, 99% washing efficiency of water soluble salts could be achieved with FGD gypsum. The gypsum qualities required for wallboard manufacturing were met by washed filter cake generated from slurry containing Cl^- up to 80,000 ppm.

ACKNOWLEDGEMENTS

The author wishes to express sincere gratitude to the following individuals for their continued support and assistance throughout the test program.

David Mobley - Environmental Protection Agency
Robert Borgwardt - Environmental Protection Agency
Norman Kaplan - Environmental Protection Agency
Mike Maxwell - Environmental Protection Agency
Gary Rochelle - University of Texas
Even Bakke - Peabody Process Systems, Inc.
Dennis Laslo - Peabody Process Systems, Inc.
Gerald Janik - New York State Electric and Gas
John Smigelski - New York State Electric and Gas
Steve DeMarco - New York State Electric and Gas
Herb Dempsey - Acurex Corporation
Andy Murphy - Acurex Corporation

The support and cooperation of the pilot plant and analytical laboratory staff under sometimes frustrating conditions is also greatly appreciated.

Mr. David Mobley was the EPA project officer.

Mr. Dennis Laslo was the Project Coordinator for PPSI.

Professor Rochelle was retained as a technical consultant for portions of this project.

TABLE OF CONTENTS

SECTION PAGE

ABSTRACT ii

ACKNOWLEDGEMENTS iii

1 SUMMARY 1-1

1.1 Chloride Ion Effect on Limestone Scrubber Performance 1-3

1.2 Evaluation of Methods Counteracting the Effects of Calcium Chloride on SO_2 Removal Efficiency in a Limestone Scrubber 1-5

1.3 Effects of Calcium Chloride on the Performance of Lime Scrubber 1-7

1.4 Effects of Calcium Chloride on the Performance of Magnesia Enhanced Limestone Scrubbing . . . 1-7

1.5 Effects of Calcium Chloride on the Performance of DBA Enhanced Limestone Scrubbing 1-8

1.6 Washability Evaluation of Gypsum Cake Produced from High Chloride Limestone Scrubbing 1-9

2 INTRODUCTION 2-1

3 TEST FACILITIES 3-1

3.1 System Description 3-1

3.2 Test Program Objectives and Schedule 3-6

4 THEORETICAL DISCUSSION 4-1

4.1 Equilibrium pH 4-1

4.2 SO_2 Absorption 4-2

4.3 Gypsum Scale 4-8

5 CHLORIDE ION EFFECTS ON LIMESTONE SCRUBBER PERFORMANCE 5-1

5.1 Effects of Calcium Chloride 5-1

5.1.1 Effect of Cl^- on System pH 5-6

TABLE OF CONTENTS
(continued)

SECTION PAGE

5.1.2 Effect of Cl^- on SO_2 Removal 5-6

5.1.3 Effect of Cl^- on Gypsum Scaling Potential 5-16

5.1.4 Effect of Cl^- on the Solid Settling Rate 5-16

5.2 EFFECTS OF MAGNESIUM CHLORIDE 5-20

5.2.1 Natural Oxidation 5-20

5.2.2 Forced Oxidation 5-29

5.3 EFFECTS OF SODIUM CHLORIDE 5-34

5.3.1 Natural Oxidation 5-34

5.3.2 Forced Oxidation 5-40

6 EVALUATION OF CALCIUM CHLORIDE EFFECT COUNTERMEASURES 6-1

6.1 High Limestone Stoichiometry Tests 6-1

6.2 High L/G Tests 6-4

6.3 Lime Addition Tests 6-4

6.4 Organic Dibasic Acid Test 6-8

7 CALCIUM CHLORIDE EFFECTS ON LIME SCRUBBER PERFORMANCE 7-1

7.1 High Sulfur Coal Tests 7-1

7.2 Low Sulfur Coal Tests 7-5

8 EFFECTS OF CALCIUM CHLORIDE ON MAGNESIA ENHANCED LIMESTONE SCRUBBER PERFORMANCE 8-1

8.1 Effect of Cl^- on Depletion of SO_3^{2-} and M_gSO_3 8-2

8.2 Effect of Calcium Chloride Accumulation 8-2

TABLE OF CONTENTS
(continued)

SECTION		PAGE
9	CALCIUM CHLORIDE EFFECTS ON DBA ENHANCED LIMESTONE SCRUBBER PERFORMANCE	9-1
	9.1 Calcium Chloride Effects on System Performance	9-2
	9.2 Effects of Calcium Chloride on DBA Degradation and Coprecipitation Rates	9-7
10	WASHABILITY EVALUATION OF GYPSUM CAKE PRODUCED FROM HIGH CHLORIDE LIMESTONE SCRUBBING	10-1
	10.1 Filter Media Evaluation	10-1
	10.2 Quality of Gypsum Evaluated	10-4
	10.3 Gypsum Washability Evaluation	10-6
	NOTATION (All Sections)	10-16
	REFERENCES (All Sections)	10-18
	APPENDIX A	A-1
	APPENDIX B	B-1

LIST OF FIGURES

FIGURE		PAGE
3-1	Flow diagram for single-loop natural oxidation tests in EPA/IERL's 0.1 MW limestone pilot plant system . .	3-2
3-2	Flow diagram for the in-loop forced oxidation tests in EPA/IERL's 0.1 MW limestone pilot plant system . .	3-3
3-3	Schedule for EPA/PPSI High Dissolved Solids Test Program	3-8
4-1	Calculated liquid phase mass transfer resistance vs. Cl^- concentration	4-6
5-1	Comparison of natural and forced oxidation hold tank pH's of calcium chloride tests	5-7
5-2	Comparison of natural oxidation hold tank pH data of calcium chloride tests with calculated response . . .	5-8
5-3	Comparison of natural and forced oxidation SO_2 removal efficiencies as a function of slurry chloride concentration for calcium chloride tests	5-9
5-4	r vs. chloride concentration for calcium chloride tests	5-14
5-5	Calcium chloride effect on limestone SO_2 scrubber performance: Hold tank calcium sulfate saturation vs. Cl^- concentration	5-17
5-6	Calcium chloride effect on limestone SO_2 scrubber performance: Scrubber effluent calcium sulfate saturation vs. Cl^- concentration	5-18
5-7	Calcium chloride effect on natural oxidation limestone SO_2 scrubber performance: minimum solids settling rate observed vs. Cl^- concentration	5-19
5-8	Calcium chloride effect on limestone SO_2 scrubber performance: solids settling rate observed vs. Cl^- concentration	5-21
5-9	Comparison of natural oxidation SO_2 removal efficiencies as a function of slurry chloride concentration	5-23
5-10	Comparison of natural oxidation hold tank pH's as a function of slurry chloride concentration	5-25
5-11	Comparison of forced oxidation SO_2 removal efficiencies as a function of slurry chloride concentration	5-27

LIST OF FIGURES
(continued)

FIGURE		PAGE
5-12	Comparison of forced oxidation hold tank pH's as a function of slurry chloride concentration	5-32
5-13	Comparison of natural oxidation SO_2 removal efficiencies as a function of slurry chloride concentration	5-33
5-14	Comparison of natural oxidation hold tank pH's as a function of slurry chloride concentration	5-36
5-15	Comparison of forced oxidation SO_2 removal efficiencies as a function of slurry chloride concentration	5-37
5-16	Comparison of forced oxidation hold tank pH's as a function of slurry chloride concentration	5-39
6-1	Limestone stoichiometric ratio required for 80% SO_2 removal vs. Cl^- concentration with natural oxidation	6-3
6-2	Effect of L/G ratio on SO_2 removal with natural oxidation	6-6
6-3	Flow diagram for two-hold-tank lime addition test . .	6-9
6-4	Scrubber performance with lime addition	6-11
6-5	Effect of organic acid concentration on sulfur dioxide removal at 50,000 ppm chloride by Monsanto DBA addition	6-14
6-6	Organic acid concentrations required to maintain 80% SO_2 removal efficiency at high chloride ion concentrations	6-17
7-1	Effect of chloride ion on the SO_2 removal efficiency of RTP lime scrubber	7-4
7-2	Chloride ion effect on system pH of RTP lime scrubber	7-6
7-3	Lime stoichiometry for high sulfur coal tests . . .	7-7
8-1	Effect of chloride ion on the SO_2 removal efficiency of a magnesia enhanced limestone scrubber	8-5

LIST OF FIGURES
(continued)

FIGURE		PAGE
8-2	Effect of chloride ion on the hold tank pH of a magnesia enhanced limestone scrubber	8-6
8-3	Comparison of natural oxidation hold tank pH's as a function of calcium and magnesium ion concentrations.	8-7
9-1	DBA required to reach 90% SO_2 removal at high chloride concentrations	9-5
9-2	Chloride effect on hold tank pH of DBA enhanced limestone scrubber	9-6
9-3	DBA required to reach 90% SO_2 removal at high chloride concentrations	9-10
9-4	Chloride effect on hold tank pH of DBA enhanced limestone scrubber	9-11
9-5	Overall material balance for run of N3-4A	9-16
9-6	Overall material balance fo run F5-4A	9-17
10-1	Performance of belt filter counter-current washing at 5 wash displacement water	10-14

LIST OF TABLES

TABLE		PAGE
3-1	Results of Fredonia Limestone Wet Sieve Analysis Used for EPA/PPSI High Chloride Tests	3-5
3-2	Analytical Methods Employed in EPA/IERL FGD Pilot Plant Lab	3-5
4-1	Calculated Effect of $CaCl_2$ Accumulation on Total Dissolved Alkalinity	4-5
5-1	Operating Conditions of Natural Oxidation Calcium Chloride Tests	5-2
5-2	Operating Conditions of Forced Oxidation Calcium Chloride Tests	5-3
5-3	Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Natural Oxidation Calcium Chloride Tests	5-4
5-4	Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Forced Oxidation Calcium Chloride Tests	5-5
5-5	Operating Conditions of Low SO_2 Make-per-pass and Low Limestone Stoichiometry Calcium Chloride Tests .	5-11
5-6	Operating Conditions of Low Sulfur Coal Calcium Chloride Tests	5-12
5-7	Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Composition for Low Sulfur Coal and Low SO_2 Make-Per-Pass Calcium Chloride Tests	5-13
5-8	Operating Conditions for Natural Oxidation Magnesium Chloride Tests	5-22
5-9	Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analyses for Natural Oxidation Magnesium Chloride Tests	5-23
5-10	Comparison of Calcium Sulfate Saturation Levels Between Calcium and Magnesium Chloride Tests	5-28
5-11	Operating Conditions for Forced Oxidation Magnesium Chloride Tests	5-30
5-12	Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analyses for Forced Oxidation Magnesium Chloride Tests	5-31

LIST OF TABLES
(continued)

TABLE PAGE

5-13 Operating Conditions for Natural Oxidation Sodium Chloride Tests 5-35

5-14 Comparison of Calcium Sulfate Saturation Levels for Sodium Chloride Tests 5-38

5-15 Operating Conditions for Forced Oxidation Sodium Chloride Tests 5-41

5-16 Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Forced Oxidation Sodium Chloride Tests 5-42

6-1 Operating Conditions of High Limestone Stoichiometry Calcium Chloride Tests with High SO_2 Make-per-pass . . 6-2

6-2 Operating Conditions of High Limestone Stoichiometry Calcium Chloride Tests with Low SO_2 Make-per-pass . . 6-5

6-3 Average Scrubber Performance for L/G Test 6-7

6-4 Operating Conditions of Lime Addition Tests 6-10

6-5 Operating Conditions of Natural Oxidation DBA Effectiveness Tests 6-13

6-6 Operating Conditions of Natural Oxidation DBA Effectiveness Tests 6-15

6-7 Operating Conditions of Forced Oxidation DBA Effectiveness Tests 6-16

7-1 Operating Conditions of High Chloride Lime Tests Under High Sulfur Coal Conditions 7-2

7-2 Summary of Liquor Analysis for High Chloride Lime Tests Under High Sulfur Coal Conditions 7-3

8-1 Major Operating Conditions of Magnesia Enhanced Limestone Tests 8-3

8-2 Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Composition of Magnesia Enhanced Limestone Tests 8-4

9-1 Operating Conditions for Natural Oxidation DBA Enhanced Limestone Tests 9-3

LIST OF TABLES
(continued)

TABLE		PAGE
9-2	Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Natural Oxidation DBA Enhanced Limestone Tests	9-4
9-3	Operating Conditions for Forced Oxidation DBA Enhanced Limestone Tests	9-8
9-4	Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Forced Oxidation DBA Enhanced Limestone Tests	9-9
9-5	Operating Conditions for Long Term DBA Material Balance Tests	9-13
9-6	Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Long Term DBA Material Balance Tests	9-14
9-7	Comparison of Unaccountable Organic Acid Losses at RTP Limestone FGD Pilot Plant	9-19
10-1	Tentative Specification of FGD Byproduct Gypsum by Wallboard Manufacturers(26)	10-2
10-2	Filter Medias Evaluated	10-3
10-3	Results of Filter Media Evaluations Tests	10-5
10-4	Summary of Cake Washability Test Conditions With 50,000 ppm Slurry Chloride Concentration (Run F5-1A).	10-7
10-5	Results of Cake Washability Test with 50,000 ppm Slurry Chloride Concentration	10-8
10-6	Summary of Cake Washability Test Conditions with Slurry Chloride Concentration at 80,000 ppm (Run F8-1A)	10-10
10-7	Results of Cake Washability Test with 80,000 ppm Slurry Chloride Concentration	10-11
10-8	Summary of Cake Washability Test Conditions with 120,000 ppm Slurry Chloride Concentration (Run F12-1A)	10-12
10-9	Results of Cake Washability Test with Slurry 120,000 ppm Slurry Chloride Concentration	10-13
10-10	Comparison of Gypsum Qualities	10-15

SECTION 1

SUMMARY

This is the final report of a pilot plant test program co-sponsored by Peabody Process Systems, Inc. (PPSI) and the U.S. Environmental Protection Agency's (EPA) Industrial Environmental Research Laboratory (IERL) to test the chloride ion (Cl^-) effects on wet flue gas desulfurization (FGD) system performance. New York State Electric and Gas also participated in test planning and data review during the early stages of testing. This report covers the entire test period from September 1981 through June 1983. The test facility is located at Research Triangle Park (RTP), North Carolina. Acurex Corporation is the major contractor and facility operator.

Chloride ion concentrations in the scrubbing liquor exceeding 18,000 ppm* are possible with tightly closed water loops in FGD systems. If closed-loop operation is assumed (i.e. the only water leaving the FGD system is through evaporation and as filter cake moisture), material balance calculations indicate total dissolved solids (TDS, usually the combination of calcium, magnesium and sodium salts) can be accumulated to levels exceeding 50,000 ppm(1,2) for high sulfur coals. Forced oxidation intensifies the TDS accumulation through improved cake dewatering. Dissolved solids can reach worst case levels in excess of 150,000 ppm(1,2). The major source of chlorides can be from the coal, as HCl in the flue gas, or from chlorides in the makeup water. The latter is especially important if cooling tower blowdown is utilized. In order to evaluate the effects of Cl^- on FGD system performance, a test program was developed to conduct pilot plant tests under simulated high chloride conditions.

---

*One ppm is equivalent to one mg/l.

The pilot plant was initially run without chlorides (i.e. chloride was not intentionally added, however, a low level of background chloride was present at relatively insignificant levels) in order to establish the base case for later comparison. Chloride ion concentration in the system was then set by adding calcium chloride, magnesium chloride, and/or sodium chloride to the hold tank. Constant stoichiometry (the molar ratio of calcium carbonate added to sulfur dioxide absorbed) was manually maintained when limestone was used as the reagent. Manual hold tank pH control was utilized when lime was the reagent. The Cl^- effects on system performance were obtained by comparing the data with and without chloride addition. Major areas of testing during the reporting period were:

- Chloride ion effects on limestone scrubber performance
  - Effects of calcium chloride
  - Effects of magnesium chloride
  - Effects of sodium chloride
  - Effects of calcium chloride combined with magnesium or sodium chloride
- Evaluation of methods counteracting the effects of calcium chloride on SO_2 removal efficiency in a limestone scrubber
- Effects of calcium chloride on lime scrubber performance
- Effects of calcium chloride on the performance of magnesia enhanced limestone scrubbing
- Effects of calcium chloride on the performance of DBA (organic dibasic acids) enhanced limestone scrubbing
- Washability evaluation of gypsum cake produced from high chloride limestone scrubbing

Major conclusions obtained from the pilot plant testing are summarized below.

1.1 CHLORIDE ION EFFECT ON LIMESTONE SCRUBBER PERFORMANCE

Pilot plant tests were conducted at Cl^- concentrations up to 180,000 ppm. Both natural and forced oxidation conditions were studied. It was found that high Cl^- concentrations resulted in significant changes in limestone scrubber performance. The extent of the change in performance was a function of several factors including the types of cations associated with the Cl^- and the scrubber operating conditions. Major conclusions from the pilot plant results are summarized as follows:

Effects of Calcium Chloride

- Scrubber hold tank pH decreased as calcium chloride concentration increased. It was shown that with natural oxidation, the change in hold tank pH followed calculated equilibrium hydrogen ion (H^+) concentrations. The drop of pH with forced oxidation was not significant until the Cl^- concentration exceeded 50,000 ppm. At the same Cl^- concentration, the observed pH decrease was less with forced oxidation than with natural oxidation.
- A decrease in SO_2 removal efficiency was observed with the increase of calcium chloride concentration for both natural and forced oxidation modes. The decrease was greater for the natural oxidation mode of operation.
- With the accumulation of calcium chloride, the estimated relative saturation of gypsum in the scrubber system increased to levels conducive to scaling. The increase was shown to be a function of calcium ion (Ca^{2+}) concentration. Also, increased scaling potential at the scrubber effluent was predicted due to increased sensitivity of the absorbing liquor to small changes in sulfate ion (SO_4^{2-}) concentration. Despite higher

calculated saturation level of gypsum, little scale was observed in the pilot plant.

- Occasional declines of solids settling rate were observed as the Cl⁻ concentration increased during the natural oxidation tests. Little effect on solids settling attributable to chlorides was observed when running in the forced oxidation mode.

Effects of Magnesium Chloride

- A drop of system pH was observed with the increase of magnesium chloride concentration. The hold tank pH decreased at a rate similar to that obtained from calcium chloride tests, especially at Cl^- concentrations below 50,000 ppm.
- With natural oxidation mode, the accumulation of magnesium chloride improved SO_2 removal efficiency when the Cl^- concentration was below 40,000 ppm. However, a significant drop of SO_2 removal efficiency was observed when the Cl^- concentration was increased above 50,000 ppm.
- With forced oxidation, no significant effects of magnesium chloride on SO_2 removal efficiency were obtained until the Cl^- concentration reached 70,000 ppm. A slight drop of SO_2 removal efficiency was observed when the Cl^- concentration increased beyond 70,000 ppm.
- Operation in the unsaturated mode with respect to gypsum was maintained at high magnesium chloride concentrations. Results of chemical analysis of slurry samples showed that calcium sulfate was below the saturation level throughout the system.

Effects of Sodium Chloride

- With natural oxidation, no significant effects on scrubber performance were observed with the accumulation of sodium chloride until the Cl^- concentration reached 50,000 ppm. However, when the chloride ion concentration exceeded 50,000 ppm, drops in both SO_2 removal efficiency and system pH were observed.

- Results of chemical analysis of slurry samples showed that unsaturated operation was sustained throughout the system.
- With forced oxidation, no significant effects of sodium chloride were obtained until the Cl^- concentration increased beyond 70,000 ppm.

Effects of Calcium Chloride Combined with Magnesium or Sodium Chloride

- One run was made with 50% of the Cl^- associated with sodium and 50% with calcium. Both the SO_2 removal efficiency and the hold tank pH results were between the data obtained with only sodium or calcium chloride.
- Another run was made with 50% of the Cl^- associated with magnesium and 50% with calcium at 40,000 ppm Cl^-(total). The drop of hold tank pH observed was similar to that obtained from runs with calcium or magnesium chloride. However, no significant changes in SO_2 removal efficiency were observed compared with the base case. It was suspected that the negative effects of calcium chloride and the positive effects of magnesium chloride were offsetting each other and resulted in zero overall effect at this particular Cl^- concentration.
- Hold tank pH data indicated that the pH value was determined by the level of calcium and magnesium ion concentrations with natural oxidation. Sodium ion (Na^+) did not affect the pH values.

1.2 EVALUATION OF METHODS COUNTERACTING THE EFFECTS OF CALCIUM CHLORIDE ON SO_2 REMOVAL EFFICIENCY IN A LIMESTONE SCRUBBER

It was shown that the most significant effect of Cl^- on SO_2 removal efficiency was observed with calcium chloride under natural oxidation. In order to counteract the effects of Cl^-, short term pilot plant tests were conducted in an effort to evaluate methods which might offset the effects of calcium chloride and thereby raise the SO_2 removal efficiency to the base case level. Major conclusions from the results of those short term tests are summarized as follows:

- The effectiveness of high limestone stoichiometry was tested with natural oxidation. An extremely high limestone stoichiometry was required to offset the depressed SO_2 removal efficiency. At 40,000 ppm Cl^-, the limestone feedrate had to be increased by more than 200 percent to reach the base case SO_2 removal. However, less excess limestone was required to offset the calcium chloride effect with low make-per-pass cases.
- A high L/G ratio was also tested. The results indicated that at 40,000 ppm Cl^-, the L/G ratio had to be doubled in order to offset the Cl^- effect on SO_2 removal efficiency during natural oxidation tests.
- Lime addition to a second hold tank was also evaluated with natural oxidation. Results indicate that a lime stoichiometric ratio of 0.7 was needed, in addition to a limestone stoichiometric ratio of 0.8, to reach the base case SO_2 removal at 50,000 ppm Cl^-.
- The mass transfer enhancement effectiveness of DBA was tested. Results indicated that DBA was very effective in counteracting the Cl^- effect in both natural and forced oxidation modes. At equivalent Cl^- concentrations, less DBA was needed with forced oxidation than with natural oxidation. Only 9.2 meq/l DBA (equivalent to 672 ppm adipic acid) was needed to compensate for the effects of 50,000 ppm Cl^- under natural oxidation, and only 9.4 meq/l (equivalent to 686 ppm adipic acid) was required to compensate for 160,000 ppm Cl^- under forced oxidation.

1.3 EFFECTS OF CALCIUM CHLORIDE ON THE PERFORMANCE OF LIME SCRUBBER

The effects of calcium chloride concentration on the performance of a lime slurry FGD process were evaluated for both high and low sulfur coal cases. The low sulfur coal condition was simulated by controlling the inlet flue gas SO_2 concentration at about 500 ppm; and high sulfur coal at about 2500 ppm. Manual control of hold tank pH instead of lime stoichiometry was utilized to minimize pH fluctuation. The test results indicated that:

- Significant effects on SO_2 removal efficiency and system pH were observed for high sulfur coal cases. Similar to results obtained with the limestone scrubber, both SO_2 removal efficiency and scrubber effluent pH dropped with the accumulation of calcium chloride.
- Only the decrease of scrubber effluent pH was observed with the increase of Cl^- concentration for low sulfur coal cases. No significant changes in SO_2 removal efficiency were obtained.

1.4 EFFECTS OF CALCIUM CHLORIDE ON THE PERFORMANCE OF MAGNESIA ENHANCED LIMESTONE SCRUBBING

Addition of magnesia to a limestone scrubber increases the concentrations of two dissolved sulfite species, SO_3^{2-} and $MgSO_3$, which react with the absorbed SO_2 and facilitate the absorption of SO_2. The accumulation of calcium chloride affects the magnesia enhanced limestone scrubbing process by reducing both SO_3^{2-} and $MgSO_3$ through chemical equilibrium effects. Pilot plant tests were conducted to evaluate the effects of calcium chloride on the performance of a magnesia enhanced limestone scrubber. The results showed that the effects of Cl^- accumulation on magnesia enhanced limestone scrubbing could be divided into two stages.

- When calcium chloride was initially added to the system, a sharp drop of SO_2 removal efficiency accompanied by a slight decrease of system pH was observed. The sharp drop of SO_2 removal efficiency reflected the drastic reduction of SO_3^{2-} and $MgSO_3$ from the scrubbing liquor by chloride addition. No significant increase of calcium ion concentration was observed during this stage.

- After most SO_3^{2-} and $MgSO_3$ were replaced by Cl^- and $MgCl_2$, further addition of calcium chloride caused increases of both calcium and Cl^- concentrations. Additional drops of both SO_2 removal efficiency and hold tank pH were observed.

1.5 EFFECTS OF CALCIUM CHLORIDE ON THE PERFORMANCE OF DBA ENHANCED LIMESTONE SCRUBBING

The operating conditions of DBA enhanced limestone scrubbing feature high SO_2 removal efficiency, low limestone stoichiometry and relatively low pH. In order to simulate DBA enhanced limestone scrubbing, base case operating parameters were set as follows: hold tank pH was controlled at 5.2, limestone stoichiometry less than 1.1 and SO_2 removal efficiency 90% for both natural and forced oxidation tests. Short term tests were utilized to evaluate the effects of Cl^- concentration. Long term runs were conducted to evaluate the DBA consumption at high Cl^- concentrations. The pilot plant test results are summarized as follows:

- Drops of SO_2 removal efficiency and system pH were observed with the increase of Cl^- concentration for both natural and forced oxidation conditions.
- Increased DBA concentrations were required in order to maintain 90% SO_2 removal efficiency with the accumulation of calcium chloride.
- Plugging and scaling problems were encountered as hard scale formed on the scrubber bottom internals while operating at Cl^- concentrations above 50,000 ppm for natural oxidation.

- A phenomena similar to "limestone blinding" was encountered while operating at a Cl^- concentration of 120,000 ppm in the forced oxidation mode.
- No effects of Cl^- on DBA degradation rate were observed.
- An increase in the DBA coprecipitation rate was observed at high calcium chloride concentrations.

1.6 WASHABILITY EVALUATION OF GYPSUM CAKE PRODUCED FROM HIGH CHLORIDE LIMESTONE SCRUBBING

The marketability of gypsum produced from forced oxidation FGD systems is affected by its purity. Gypsum generated from high chloride limestone scrubbers must be washed thoroughly to reduce the content of water soluble salts to meet the marketplace purity requirements. A belt filter with the capability of three-stage countercurrent washing was utilized to evaluate the washability of dissolved salts from the FGD gypsum. The results indicated:

- Gypsum with calcium sulfate greater than 96% and calcium carbonate less than 2% could be produced from a DBA enhanced limestone scrubber.
- With five displacements of wash water and three stage countercurrent washing, 99% washing efficiency of the water soluble salts could be achieved with FGD gypsum.
- The gypsum qualities required for wallboard manufacturing were met by the washed filter cake generated from slurry containing up to 80,000 ppm of Cl^-.

SECTION 2

INTRODUCTION

The advent of tightly closed water loops in wet FGD systems, combined with the combustion of high chloride coals and the use of cooling tower blowdown as makeup water has produced a situation where high concentrations of soluble chlorides in the absorbing liquor should be considered as a design factor.

The two primary sources of the Cl^- in FGD liquor are the chloride in the coal and makeup water, especially if cooling tower blowdown is utilized. Small amounts of chlorides may also be present in the reagents such as lime, limestone or flyash. Upon combustion of the coal, most chlorides will exist as gaseous HCl. The solid phase chlorides, detectable in boiler bottom ash and electrostatic precipitator ash (probably due to salt precipitation or sorption of HCl on alkaline flyash) are very low in concentration(3). Absorption of HCl in the FGD scrubber liquor will result in a corresponding increase in the concentration of calcium and Cl^- s as shown below, using limestone or lime as the alkali.

$$HCl_{(g)} + H_2O \longrightarrow H^+ + Cl^- + H_2O$$

$$CaCO_{3(s)} + 2H^+ \longrightarrow Ca^{2+} + CO_2 + H_2O$$

$$CaO_{(s)} + H^+ \longrightarrow Ca^{2+} + OH^-$$

However, predicting the quantity of HCl reaching the absorber is difficult since little data are available. PEDCo monitored chloride concentrations at the R. D. Morrow Station and roughly determined by calculated mass balance that 95% of the chlorides in the coal reached the absorber as HCl and 95% of the HCl was absorbed in the FGD liquor although all process streams were not measured for chlorides(4).

In order to broaden this data base, a survey of 32 utilities which own or operate 60 FGD systems characterized as having closed water loops was performed by PEDCo for PPSI(5). Detailed data on chlorides were obtained for only three systems and general chloride data were obtained for another 15 systems. For the three systems where detailed chloride data were reported, chloride concentrations of 1500 ppm (Pleasants 1 and 2; 0.04% Cl Coal), 11,000 ppm (R. D. Morrow 1 and 2; 0.11% Cl Coal), and 4200 ppm (Dallman 3; 0.11% Cl Coal) were reported. The investigation indicated little or no data exist for ash and reagent chloride analysis.

The station with the highest reported chloride concentration, R. D. Morrow, has indicated that switching from calcitic to high magnesium limestone alleviated scaling problems (assumed to be caused by the chlorides) by providing high levels of dissolved magnesium in the absorbing liquor.

The second primary source of chloride accumulation in FGD systems, makeup water, is also a source of sodium, magnesium, and other cations. Thus, chloride accumulation from makeup water may have different effects on FGD chemistry than accumulation from HCl gas absorption.

The effects of chlorides on lime/limestone flue gas desulfurization system performance have previously been studied, primarily in the range of less than 30,000 ppm, but the results are mixed:

- Bechtel(6) first reported that increased chloride concentrations improved SO_2 removal efficiency at a constant hold tank pH in the Shawnee spray tower and Turbulent Contact Absorber (TCA) with chloride concentrations approaching 20,000 ppm. Later, Bechtel's final analysis of the data(7) indicated a slight increase in SO_2 removal efficiency only on the spray tower when using lime as the alkali. Chlorides had no significant effects on SO_2 removal efficiencies in the TCA with either alkali.

- Borgwardt(8) found a decrease in the rate of limestone dissolution at 5000 and 20,000 ppm $CaCl_2$ (as Cl^-) in beaker titrations. Nitrogen sparging significantly improved the dissolution rate presumably by stripping CO_2 gas from solution.
- Borgwardt(8) also found deteriorative results due to the chlorides in EPA's IERL/RTP pilot plant using the 22.3 cm diameter TCA injected with HCl gas. Minor changes in absorber performance were noted in tests with natural oxidation at 5000 ppm Cl^- and forced oxidation tests at 22,000 ppm Cl^-; however, when chlorides were increased from 0 to 19,000 ppm in the natural oxidation mode, SO_2 removal efficiency dropped from 86% to 74% and the recycle tank pH decreased from 6.0 to 5.4.
- Rochelle(9) measured decreased limestone dissolution using a pH-stat at high concentrations of calcium chloride ($CaCl_2$) at a pH of 5.0 with nitrogen sparging. He attributed this effect to slowed H^+ diffusivity in high ionic strength solutions. Results indicated that increasing $CaCl_2$ concentrations from 0.1M to 2.0M decreased the limestone dissolution rate constant from 1.9×10^{-9} cm^2/sec to 2.94×10^{-10} cm^2/sec.
- Kobe Steel(10) indicated SO_2 removal efficiency increases with chloride concentrations as high as 30 weight percent using lime in a unique clear solution $CaCl_2$ process.
- Borgwardt(11) also studied chloride accumulation in limestone FGD scrubbers using HCl gas and simulated cooling tower blowdown (Na_2SO_4 in water saturated with gypsum) as system makeup water in EPA's pilot plant. An improvement in SO_2 removal efficiency was noted at chloride levels of 23,000 ppm and sodium levels of 12,000 ppm over the fresh water makeup base case (17,000 ppm Cl^-, and no Na^+). Borgwardt attributed the improvement to favorable ion diffusivities and equilibrium

constants. Scaling in the absorber was consistently observed at sodium levels exceeding 15,000 ppm and an SO_2 make-per-pass exceeding 8.0 mM.

- Combustion Engineering (CE) conducted pilot plant tests on a 0.4MW pilot plant. Initially, Rader(12) reported an increase in SO_2 removal efficiencies as Cl^- concentrations increased. In a subsequent report(13), CE tests indicated no effect of chloride ions on SO_2 removal efficiencies with inlet flue gas SO_2 concentrations ranging from 500 to 1500 ppm and chloride ion concentrations as high as 80,000 ppm.

Recently, extensive research and development efforts have been undertaken to further study the effects of dissolved solids on lime/limestone FGD systems:

- EPRI contracted Radian Corporation to examine the effects of TDS on SO_2 mass transfer in a bench scale absorber. Included in this work was a simulation of the PPSI/EPA pilot plant work for natural and forced oxidation.
- Dr. G. Rochelle at the University of Texas has initiated research in the theoretical modeling of slurry scrubber performance with gas/liquid mass transfer, $CaSO_3$ dissolution, and $CaCO_3$ dissolution in the presence of high concentrations of dissolved solids.
- EPRI, TVA, and Babcock and Wilcox have studied Cl^- effects in the 10MW spray tower at TVA's Shawnee test facility. Results have not been published as of this writing.

It was apparent from the literature survey that:

1. Chloride ions could have significant impacts on the performance of wet FGD systems. The conservation of water in the electric power industry demands tightly closed water loops in FGD systems which can promote the buildup of Cl^- in the recirculating scrubbing liquor. Therefore,

experimental data on Cl^- concentration effects were needed for future engineering design and scrubber operation purposes.

2. Other than calcium chloride, the effects of magnesium and sodium chloride should also be tested so that the use of cooling tower blowdown as makeup water can be evaluated.
3. Most existing data and recent experiments concentrated on conventional limestone FGD processes. The effects of Cl^- concentration on the performance of FGD processes such as magnesia enhanced and DBA enhanced limestone systems should also be investigated.

In order to broaden the data base of Cl^- effects on FGD system performance, a pilot plant test program was initiated under a cooperative agreement between PPSI and EPA in September, 1981. Test work was performed by Acurex Corporation at the EPA/IERL's 0.1 MW pilot plant. Initially, baseline performance of the pilot plant was established. The effects of calcium chloride, magnesium chloride and sodium chloride on limestone FGD system performance were then evaluated. Significant impacts of chlorides, especially calcium chloride, were indicated by the pilot plant data. The drop of SO_2 removal efficiency with the increase of calcium chloride concentration caused concerns about SO_2 emission compliance problems. Pilot plant tests were designed to evaluate methods to counteract the deleterious effects of calcium chloride on SO_2 removal efficiency. Pilot plant tests conducted included assessment of the effectiveness of high limestone stoichiometry, hydroclone, lime addition, high L/G and DBA enhancement. DBA was found a very effective mass transfer additive and only a very small amount was required to counteract the calcium chloride effects on SO_2 removal efficiency.

In 1982, PPSI and EPA continued the co-sponsored pilot plant program. Additional testing included:

- An investigation of the feasibility of producing commercial grade gypsum in the presence of high Cl^- ion concentrations,
- An examination of the effects of calcium chloride on magnesia and DBA enhanced limestone scrubbers,
- Evaluations of cations other than Ca^{2+},
- The use of lime instead of limestone as the alkali.

The pilot plant program ended in June 1983. This final report covers the entire period of high chloride pilot plant testing from september 1981 to June 1983.

SECTION 3

TEST FACILITIES

A pilot plant test program was developed to simulate full scale scrubber operation and evaluate the effects of chlorides on FGD system performance with high Cl^- concentrations in the scrubbing liquor.

3.1 SYSTEM DESCRIPTION

Two process configurations, natural and forced oxidation, shown in Figures 3-1 and 3-2 were utilized for the tests. The test facility, located at EPA/IERL's laboratories in Research Triangle Park, NC, is a three stage turbulent contact absorber (TCA) with 7.5 m^3/min flue gas capacity (0.1 MW). No flyash is present in the flue gas which is drawn from a gas-fired boiler and injected with pure SO_2 and HCl as required. The flue gas oxygen content was varied from 5 to 10 percent by adjusting the amount of boiler excess air. The flue gas CO_2 content is also a function of boiler excess air. Typical range of flue gas CO_2 concentration was 4 to 8 percent. The range of adiabatic saturation temperature was estimated to be 55 to 60°C. The oxidizer is a 30 cm diameter tower containing slurry at a depth of 5.5 m with provision for sparging with air from the tower bottom. A bleed stream of slurry from the 680 l hold tank is directed to a clarifier and then processed by a rotary drum vacuum filter to remove the precipitated waste slurry. Closed loop operation was maintained by returning all filtrate to the scrubber. The system was manually controlled in a feed forward mode by maintaining a constant stoichiometric ratio of moles of limestone added to moles of SO_2 absorbed. Feedback control to maintain constant hold tank pH was utilized when lime was the reagent. A small amount of excess reagent was also added to stoichiometrically neutralize the HCl gas absorbed.

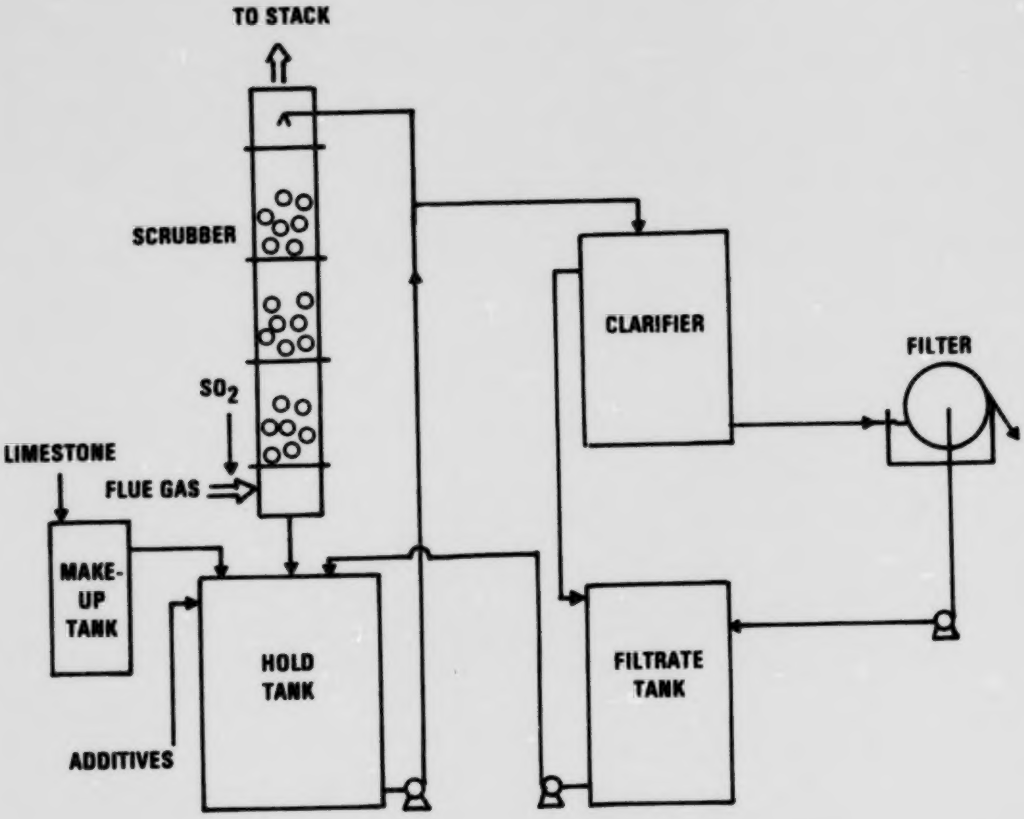


Figure 3-1. Flow diagram for single-loop natural oxidation tests in EPA/IERL's 0.1 MW limestone pilot plant system.

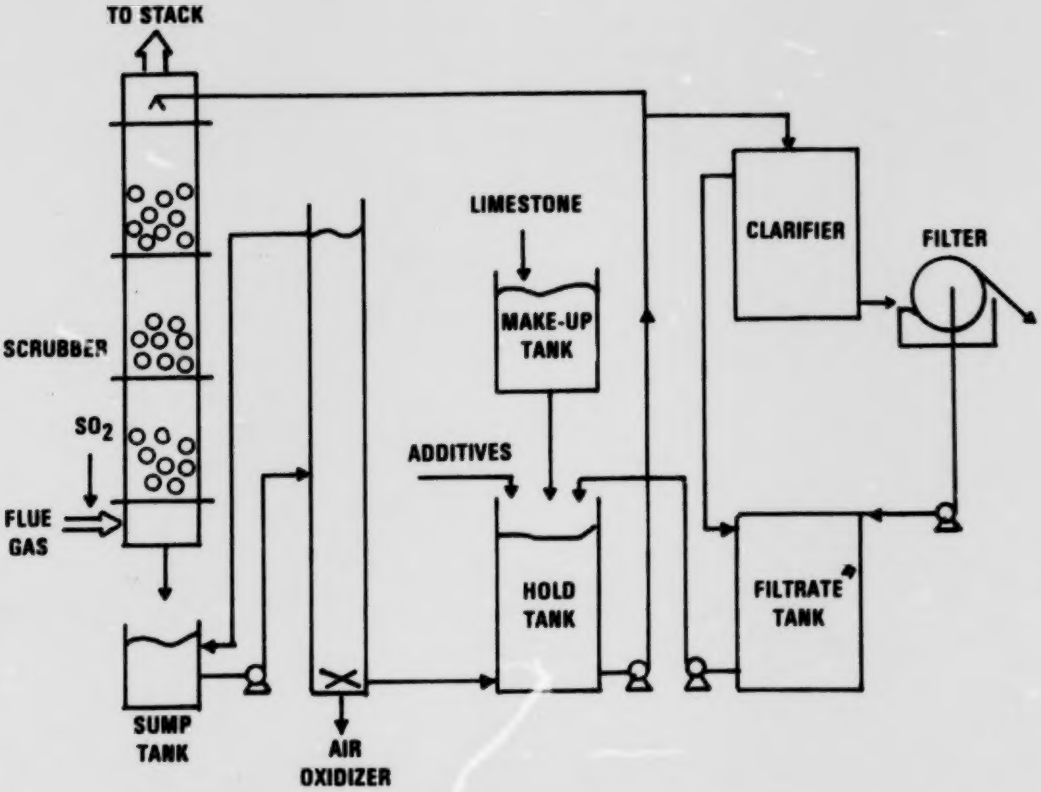


Figure 3-2. Flow diagram for the in-loop forced oxidation tests in EPA/IERL's 0.1 MW limestone pilot plant system.

Industrial grade calcium chloride, magnesium chloride or sodium chloride was added to the liquid inventory to spike the system to the desired chloride level. HCl was (at indicated times) injected into the flue gas at predetermined levels to simulate flue gas generated from high chloride coal. The limestone feed rate was adjusted manually by a trial and error method that required SO_2 removal efficiency consideration to achieve steady state stoichiometric ratios. Two grinds of Fredonia limestone, nominally 90%-325 mesh and 80%-325 mesh, were utilized. Table 3-1 lists the results of wet sieve analysis of each grind. Normally, each run consisted of at least 25 hours of continuous, stable operation, after which scrubber performance and system conditions at each chloride level were established by averaging operational data logged hourly.

The gas phase sulfur dioxide concentration at the inlet and outlet of the scrubber was monitored continuously by ultraviolet spectrophotometry (DuPont 460 SO_2 analyzer) and periodically by modified Method 8(14). The liquid phase Cl^- concentration was controlled by manual addition of chloride salts. The Cl^- concentration was monitored by a chloride specific ion electrode and checked by ion chromatography and argentometric titration. The hold tank slurry settling rate was measured in a 100 ml graduated cylinder. The initial three minute average rate of descension of the miniscus between the clear supernate and the turbid zone was reported as the solid settling rate. Liquid and solid samples were taken regularly for the major species analysis (calcium, sulfite, sulfate, carbonate, magnesium and sodium). The analytical techniques utilized for liquid/solid analysis are shown in Table 3-2.

Table 3-1. Results of Fredonia Limestone Wet Sieve Analysis Used for EPA/PPSI High Chloride Tests

Nominal Grind	-325 mesh	-250 mesh	Weight Percent -200 mesh	-100 mesh	-70 mesh
90%-325 mesh(a)	93.05	97.9	98.7	99.9	99.9
80%-325 mesh(b)	79.6	89.1	91.8	98.4	99.2

(a) Used by tests NB-1, FB-1, N2-1, N2-2, N3-1, N3-2, N4-1, N4-2, N5-1, N5-1L, N5-2L, N5-3L, N5-4L and N5-5L

(b) Used by remaining tests

Table 3-2. Analytical Methods Employed in EPA/IERL FGD Pilot Plant Lab

Specie Quantified	Method
Total Sulfur	Oxidized to SO_4^{2-} by H_2O_2 Analyze SO_4^{2-} by IC(a)
Total Oxidizable Sulfur	Iodometric titration
Carbonate	CO_2 evaluation, alkali trap
Chloride	IC, specific ion electrode and argentometric titration
Adipate	IC
Total Organic Acid	Silicic acid titration
Sodium	AAS(b), IC
Calcium	AAS, EDTA titration, IC
Magnesium	AAS, EDTA titration, IC

(a) Ion chromatography
(b) Atomic absorption spectroscopy

3.2 TEST PROGRAM OBJECTIVES AND SCHEDULE

The objectives of the chloride test program were:

- To establish the baseline scrubber performance without chloride addition
- To investigate the effects of calcium chloride on limestone scrubber performance under both natural and forced oxidation conditions at various inlet SO_2 concentrations, SO_2 make-per-pass levels and limestone stoichiometries
- To evaluate methods of counteracting the effects of calcium chloride on the SO_2 removal efficiency of the limestone scrubber
- To evaluate the effects of magnesium chloride on limestone scrubber performance under both natural and forced oxidation conditions
- To investigate the effects of sodium chloride on limestone scrubber performance under both natural and forced oxidation conditions
- To evaluate the effects of calcium chloride combined with either magnesium or sodium chloride on limestone scrubber performance
- To investigate the effects of calcium chloride on lime scrubber performance for both high and low sulfur coal cases
- To evaluate the effects of calcium chloride on magnesia enhanced limestone scrubber performance
- To investigate the effects of calcium chloride on DBA enhanced lime stone scrubber performance
- To evaluate DBA degradation and coprecipitation rates at high calcium chloride concentrations
- To evaluate the washability of gypsum filter cake produced at high Cl^- conditions in the limestone scrubber

A bar chart of the high chloride pilot plant test program, showing time spent on each of the defined objectives, is presented in Figure 3-3.

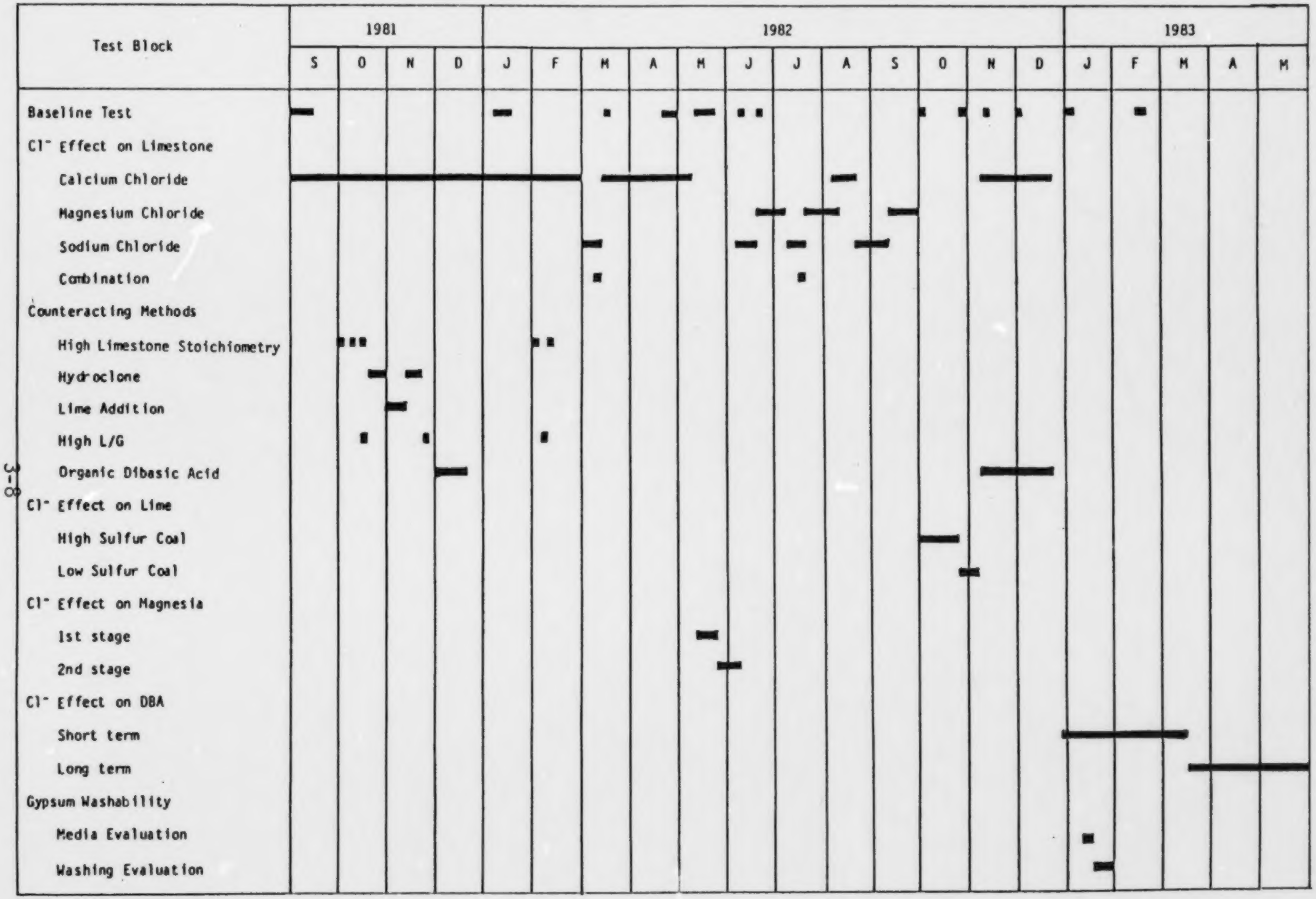


Figure 3-3. Schedule for EPA/PPSI High Dissolved Solids Test Program.

SECTION 4

THEORETICAL DISCUSSION

When HCl in flue gas is absorbed by limestone slurry and accumulates in the scrubbing liquor as chloride anions (Cl^-), the liquid phase calcium cation (Ca^{2+}) concentration increases correspondingly to maintain ionic balance in the absence of other cations. At a constant limestone stoichiometric ratio, defined as moles of limestone added per mole of SO_2 absorbed, increasing the Ca^{2+} concentration affects system chemistry and scrubber performance significantly. Literature survey indicated higher Ca^{2+} concentrations have resulted in lower equilibrium pH and increased gypsum scaling potential.

4.1. EQUILIBRIUM pH:

In a limestone FGD system, the equilibrium Ca^{2+} concentration is related to H^+ concentration by the following relationships:

$$CaCO_{3(s)} + 2H^+_{(aq)} \longrightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \qquad (4\text{-}1)$$

$$\text{for which } A_{Ca^{2+}} = K \frac{A^2_{H^+}}{P_{CO_2}} \qquad (4\text{-}2)$$

Therefore, at constant CO_2 partial pressure, the H^+ concentration increases (i.e. the pH decreases) as the Ca^{2+} concentration increases.

Under natural oxidation conditions, P_{CO_2} of the limestone scrubbing liquor is partially limited by the flue gas CO_2 concentration and can be assumed to be relatively constant. Therefore, even a finite approach to equilibrium will require a pH decrease at higher Ca^{2+} concentration.

However, under in-loop forced oxidation conditions, equilibrium pH can not be directly related to Ca^{2+} concentration by Equations (4-1) and (4-2) since oxidizaer air not only oxidizes dissolved SO_2 but also strips off carbon dioxide which makes P_{CO_2} and the system pH primarily a function of the sparger air rate. Therefore, less of an effect of calcium chloride on equilibrium pH was expected with forced oxidation.

4.2 SO_2 ABSORPTION

The absorption of SO_2 from flue gas by limestone slurry can be regarded as gas absorption accompanied by chemical reactions in the liquid phase. Since the SO_2 absorption rate is primarily controlled by liquid phase mass transfer resistance(15) and the gas phase SO_2 diffusion rate is unaffected by the presence of dilute HCl gas, the major effect of Cl^- on the SO_2 mass transfer rate was expected to occur in the liquid phase.

The liquid side mass transfer rate of SO_2 across the gas-liquid interphase can be expressed as a molar flux:

$$N = \phi k_l (C^i_{SO_2} - C^o_{SO_2}) \qquad (4\text{-}3)$$

The mass transfer enhancement factor, ϕ, is a function of the liquid phase chemical reactions. The liquid phase mass transfer coefficient, k_l, is related to the diffusion rate and the liquid phase SO_2 concentration, C_{SO_2}, is a function of the solubility of sulfur dioxide. As will be shown, each of these parameters is affected by the increase of Cl^- concentrations.

The concentration of SO_2 at the gas-liquid interface, $C^i_{SO_2}$, can be related to the partial pressure of SO_2 at the interface, $P^i_{SO_2}$, by an expression similar to Henry's Law:

$$\alpha \cdot P^i_{SO_2} = C^i_{SO_2} \qquad (4\text{-}4)$$

The correlation constant, α, is a function of liquid phase ionic strength, I, which increases with the accumulation of Cl^-:

$$\log \frac{\alpha}{\alpha_w} = k\, I\ , \qquad \text{with } k = 0.019 \text{ for } CaCl_2^{(16)} \tag{4-5}$$

and

$$I = \frac{\Sigma n_j^2 C_j}{2} \tag{4-6}$$

According to the penetration theory, the liquid phase mass transfer coefficient, k_l, is proportional to the square root of the SO_2 diffusivity, D. Accumulation of calcium chloride affects the diffusivity (thus k_l) through the change of liquid viscosity:(17)

$$\log \frac{D}{D_w} = -0.637 \log (1 + 0.2775\, C_{CaCl_2}) \tag{4-7}$$

Equations (4-5) and (4-7) indicate that the increase of Cl^- concentration enhances the solubility but decreases the diffusivity of dissolved SO_2. In terms of the SO_2 mass transfer rate, Equation (4-3), these two factors tend to offset each other and a minimal effect, due to diffusivity and solubility change, on SO_2 absorption rate is expected. Calculations indicate that an increase of Cl^- concentration from 200 ppm to 100,000 ppm only changes the product of k_l and $C^i_{SO_2}$ by +8 percent.

However, the mass transfer enhancement factor, φ, can change significantly when calcium chloride accumulates. This can best be explained by examining the various reactions which occur in solution. First, the hydrolysis reaction is expected to occur when SO_2 is dissolved in water:(18)

$$SO_2 + H_2O \longrightarrow H^+ + HSO_3^- \tag{4-8}$$

In addition, alkaline species derived from dissolved limestone react with SO_2 to form bisulfite ions. More than ten chemical reactions involving dissolved

SO_2 and alkalinities have been identified by Hatfield and Slack.(19) In limestone scrubbers, the most important are:

$$SO_2 + SO_3^{2-} + H_2O \longrightarrow 2HSO_3^- \tag{4-9}$$

$$SO_2 + CaSO_3 + H_2O \longrightarrow 2HSO_3^- + Ca^{2+} \tag{4-10}$$

$$SO_2 + HCO_3^- \longrightarrow HSO_3^- + CO_2 \tag{4-11}$$

$$SO_2 + CaHCO_3^+ \longrightarrow HSO_3^- + Ca^{2+} + CO_2 \tag{4-12}$$

Rochelle and King(15) suggested that ϕ is related to total alkalinity as

$$\phi = 1 + \frac{D_A}{D} \frac{C_A}{C^i_{SO_2}} \tag{4-13}$$

If we define the alkalinity concentration, C_A, as the total concentration of SO_3^{2-}, $CaSO_3$, HCO_3^-, and $CaHCO_3^+$; the Cl^- effect on C_A can be estimated by the Bechtel Modified Radian Equilibrium computer program.(20,21) Table 4-1 lists the calculated concentrations of each alkaline species and the estimated total alkalinity at various chloride levels. It is evident that the total alkalinity is reduced by more than 40 percent with the accumulation of Cl^- from 200 ppm to 20,000 ppm. With the assumption that D_A/D equals 1 and C_{SO_2} is negligible compared with $C^i_{SO_2}$, the relative liquid side mass transfer resistance, $\frac{1}{\phi k_l \alpha}$, at various Cl^- concentrations, can be estimated by Equations (4-5), (4-7) and (4-13) at a given interfacial SO_2 partial pressure. Figure 4-1 indicates that the liquid side mass transfer resistance increases by more than 50 percent when the chloride concentration increases from 200 ppm to 20,000 ppm at 0.001 atm $P^i_{SO_2}$. Since the SO_2 absorption rate is primarily controlled by liquid phase mass transfer resistance, a corresponding decrease in SO_2 removal efficiency is expected with the accumulation of Cl^- in the scrubbing liquor.

Table 4-1

Calculated Effect of $CaCl_2$ Accumulation on Total Dissolved Alkalinity

		Dissolved Alkalinity (mM)		
Ion	Base Case*	Chloride Concentration (ppm x 10^{-3}) 20	50	100
HCO_3^-	2.73	0.705	0.422	0.212
$CaHCO_3^+$	0.152	0.789	1.03	1.12
SO_3^{2-}	0.218	0.024	0.01	-
$CaSO_3$	0.744	0.646	0.52	0.363
Total	3.84	2.16	1.98	1.69

*Assume: $CaCO_3$ saturation = 0.25

$CaSO_3$ saturation = 1.5

pH = 6.0

Ca^{2+} = 250 ppm

P_{CO_2} = 0.2 atm

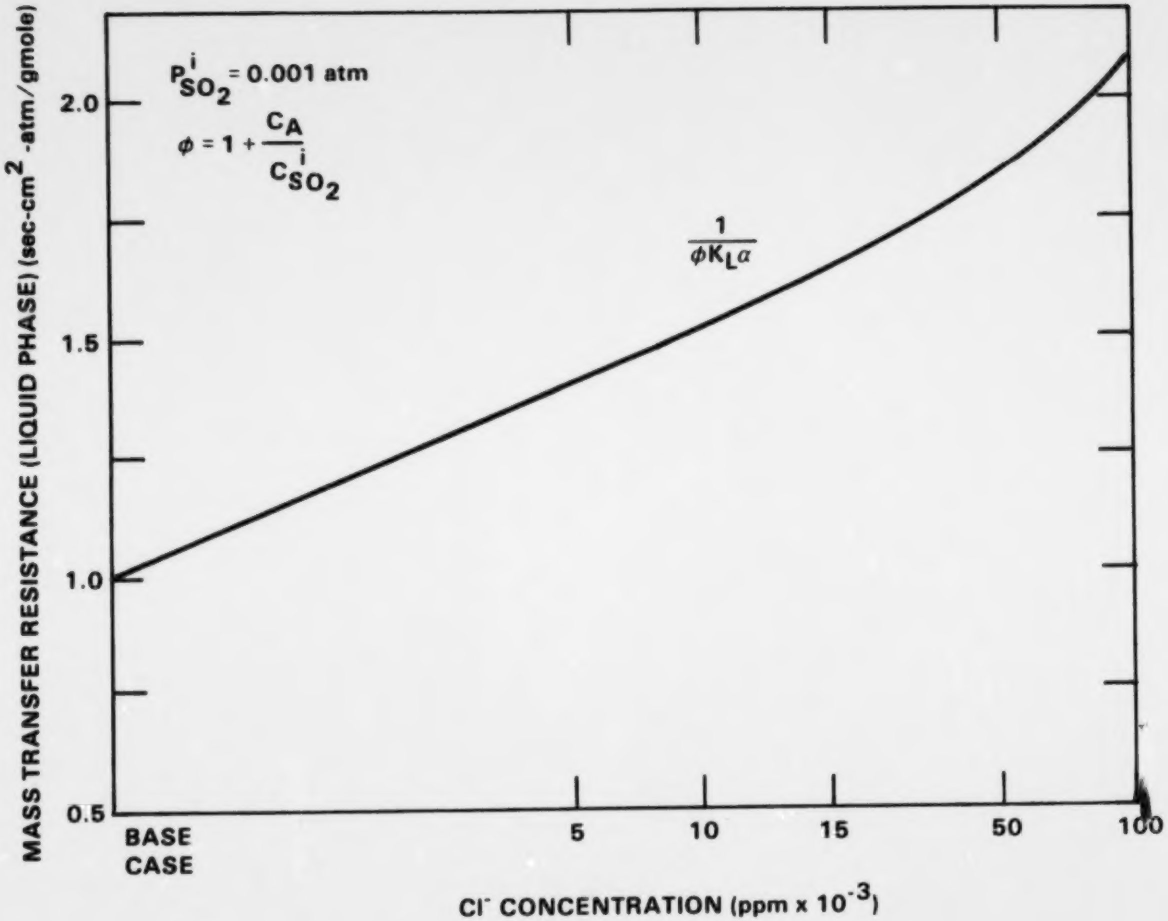


Figure 4-1. Calculated liquid phase mass transfer resistance vs. Cl$^-$ concentration.

As shown in Table 4-1 and Figure 4-1, the decrease of total alkalinity or, the increase of mass transfer resistance, above 20,000 ppm Cl$^-$ is not as significant as below 20,000 ppm Cl$^-$. However, the trend indicates that the SO_2 removal efficiency should continue to drop with further increase of Cl$^-$ concentration beyond 20,000 ppm.

In order to evaluate the effect of Cl$^-$ on SO_2 removal efficiency across the scrubber, an integrated mass transfer model developed from a differential material balance was utilized.

The rate of SO_2 absorption in the scrubber can be written for a differential height as follows:

$$\frac{-G}{P_T} \frac{dP_{SO_2}}{d_Z} = K_G a \left(P_{SO_2} - \overset{o}{P}_{SO_2}\right) \qquad (4\text{-}14)$$

where $K_G a = \left(\frac{1}{k_g a} + \frac{1}{\alpha\phi k_l a}\right)^{-1}$ and, (4-15)

$$\overset{o}{P}_{SO_2} = \overset{o}{C}_{SO_2}$$

Wang and Burbank(22) simplified equations (4-14) and (4-15) for limestone scrubbing. Since $\overset{o}{P}_{SO_2} << P_{SO_2}$ and the liquid side resistance is dominant (i.e. $\alpha\phi k_l a << k_g a$), after integration equation (4-14) yielded,

$$SO_2 \text{ removal efficiency} = 1 - EXP\ (\alpha\phi k_l a\ Z/G) \qquad (4\text{-}16)$$

or, taking the logorithm of both sides,

$$\ln\ (1 - SO_2 \text{ removal efficiency}) = \frac{-\alpha\phi k l a}{G} \qquad (4\text{-}17)$$

In order to compare the effect of Cl$^-$ on SO_2 mass transfer, the ratio of equation (4-17) with high Cl$^-$ concentration (labeled as h) to equation (4-17) without Cl$^-$ accumulation (labeled as b for base case), provides the following:

$$r = \frac{[\ln\ (1 - SO_2 \text{ removal efficiency}]_h}{[\ln\ (1 - SO_2 \text{ removal efficiency}]_b} \qquad (4\text{-}18)$$

Therefore, equation (4-18) can be utilized to normalize the Cl^- effects and compare the Cl^- effects on SO_2 removal efficiency under various operating conditions (or different base cases). The values of r should be less than 1.0 if the high Cl^- concentrations reduce SO_2 removal efficiency.

4.3 GYPSUM SCALE

Calcium chloride accumulation has two major impacts on gypsum scaling potential in a limestone scrubber: (1) transformation of the scrubber operation from a subsaturated to a supersaturated mode with respect to calcium sulfate, and (2) causing a substantial increase in relative saturation of gypsum across the scrubber.

In order to minimize the scaling potential, a limestone scrubber is preferentially operated in a subsaturated mode with respect to gypsum, or:

$$\text{R.S. (Relative Saturation)} = \frac{A_{Ca^{2+}} \cdot A_{SO_4^{2-}}}{K_{sp}} < 1.0 \qquad (4\text{-}19)$$

To maintain the subsaturation mode, all sulfate resulting from oxidation in the scrubber must coprecipitate with calcium sulfite to form a "solid solution". The coprecipitation mechanism is equilibrium controlled and has been empirically correlated$^{(23)}$, yielding the relationship:

$$\left(\frac{SO_4^{2-}}{SO_3^{2-}}\right)_{solid} = C' A^x_{Ca^{2+}} \cdot A^y_{SO_4^{2-}} \qquad (4\text{-}20)$$

where $y > x$

Substituting Equation (4-19) into Equation (4-20)

$$\left(\frac{SO_4^{2-}}{SO_3^{2-}}\right)_{solid} = C'' \frac{(R.S.)^y}{\left(A_{Ca^{2+}}\right)^z} \qquad (4\text{-}21)$$

where $C'' = C'(K_{sp})^y$
$z = y - x$
$z > 0$

The expression, $\left(\frac{SO_4^{2-}}{SO_3^{2-}}\right)_{solid}$, represents the sulfate to sulfite ratio in the solid and should be constant at a given oxidation level. Equation (4-21) indicates that if the oxidation level is fixed, the gypsum relative saturation will increase with the accumulation of calcium (as a result of the increase in Cl^-) in order to maintain a constant SO_4^{2-} to SO_3^{2-} ratio in solids. In other words, higher gypsum scaling potential will result from the increase of calcium chloride. Furthermore, in the presence of a significant concentration of Cl^-, the subsaturated mode may be unobtainable and the scrubber will be forced into a supersaturated mode of operation.

According to this model, another impact of calcium chloride accumulation on scaling is a potential increase of the gypsum relative saturation across the absorber. Equation (4-19) indicates that with high Ca^{2+} concentrations, the gypsum relative saturation level becomes very sensitive to changes in the sulfate concentration. At a high value of $A_{Ca^{2+}}$, a very small increase in the concentration of sulfate in the absorber (due to oxidation by flue gas oxygen) may result in a significant rise in the calcium sulfate saturation level and may produce gypsum scale in the bottom of the absorber.

SECTION 5

CHLORIDE ION EFFECTS ON LIMESTONE SCRUBBER PERFORMANCE

The system chemistry of Cl^- accumulation emerged as a potentially serious performance problem at limestone slurry scrubbers being designed with very tightly closed water balances. The co-sponsored (PPSI and EPA) test program focused on the evaluation of Cl^- effects on limestone scrubber performance.

System performance was evaluated in terms of SO_2 removal efficiency, system pH, gypsum scaling potential and solids quality. The effects of Cl^- associated with three different cations, Ca^{2+}, Mg^{2+} and Na^+, were tested separately. Tests were also conducted to investigate the combined effects of various cations.

5.1 EFFECTS OF CALCIUM CHLORIDE

Operating conditions and summaries of scrubbing liquor analysis are shown in Tables 5-1 to 5-4 for both natural and forced oxidation tests.

Tests without the addition of HCl and $CaCl_2$ provided the base case scrubber performance data. Base case SO_2 removal efficiency of 79% and hold tank pH of 6.0 were reached with the natural oxidation mode (Table 5-1, run NB-1). With forced oxidation, the base case SO_2 removal efficiency of 84% was obtained with a hold tank pH of 6.6 (Table 5-2, run FB-1). Another run (FB-3) was made at a lower pH (5.9) with 80% SO_2 removal. The solids content of the recycle slurry was maintained at 10 percent. Subsaturated operation with respect to gypsum was obtained under natural oxidation with a relative saturation level of 50 percent in the hold tank and 70 percent in the scrubber effluent (Table 5-3, run NB-1). The filter cake averaged 53 percent solids with natural oxidation and 78 percent solids with forced oxidation, and corresponded to hold tank slurry settling rates of 0.5 and 4.9 cm/min, respectively.

Table 5-1. Operating Conditions of Natural Oxidation Calcium Chloride Tests

Test	NB-1	N2-1	N3-1	N4-1	N5-1	N5-9	N10-1	N10-3	N10-4
Cl^- Concentration, ppm	Base case	20500.0	31400.0	40530.0	50100.0	50000.0	100,000.0	100000.0	100,000.0
L/G, liters/meter^3	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Absorber feed pH	6.0	5.3	5.2	5.1	4.9	5.1	4.6	4.8	4.7
Absorber effluent pH	5.6	4.9	4.9	4.6	4.5	4.6	4.0	4.1	4.1
SO_2 inlet conc., ppm	2570	2570	2570	2610	2570	2450	2510	2480	2480
SO_2 removal efficiency, %	79.0	73.0	70.0	62.0	58.0	61.0	32.7	48.0	46.0
SO_2 make-per-pass, mole/liter	8.4	7.8	7.5	6.7	6.2	6.6	3.44	4.9	4.8
Limestone stoichiometry	1.25	1.32	1.33	1.39	1.39	1.4	1.92	1.41	1.43
Solids settling rate, cm/min	0.5	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.1
Height packing, cm	53.3	53.3	53.3	53.3	53.3	53.3	53.3	53.3	53.3
Flue gas O_2, %	10.4	9.8	9.1	11.3	9.5	6.2	10.3	6.0	5.9
Oxidation, %	12.6	16.3	16.5	13.6	11.8	19.3	33	-	25.4
Filter cake solids conc., %	53.0	47.0	49.0	52.0	52.3	49.7	50.9	49.5	49.4

Table 5-2. Operating Conditions of Forced Oxidation Calcium Chloride Tests

Test	FB-1	FB-3	F2-1	F5-1	F8-1	F18-1
Cl- concentration, ppm	Base case	Base case	20000.0	50200.0	80130.0	179700.0
L/G, liters/meter^3	8.0	8.0	8.0	8.0	8.0	8.0
Absorber feed pH	6.6	5.9	5.8	5.7	5.5	5.2
Absorber effluent pH	5.7	5.1	4.9	4.6	4.4	4.1
SO_2 inlet conc., ppm	2480	2470	2330	2460	2480	2500
SO_2 removal efficiency, %	84.0	80.0	79.0	73.0	66.0	35.0
SO_2 make-per-pass, mole/liter	8.7	8.4	8.1	7.7	7.0	3.7
Limestone stoichiometry	1.22	1.16	1.18	1.22	1.25	1.64
Filter cake solids conc., %	73.0	78.2	78.6	77.2	78.5	79.4
Solids settling rate, cm/min	3.1	4.9	4.5	4.2	4.3	0.9
Height packing, cm	53.3	53.3	53.3	53.3	53.3	53.3
Flue gas O_2, %	9.9	8.8	9.0	9.4	9.0	10.6
Oxidation, %	88.0	99.2	98.3	98.1	96.6	98.6

Table 5-3. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Natural Oxidation Calcium Chloride Tests

Test	NB-1		N2-1		N3-1		N4-1		N5-1		N10-3	
Component, ppm	HT	SE	HT	SE	HT	SE	HT	SE	HT	SE	HT	SE
Ca	385	478	10700	10900	15600	16500	22050	21800	26600	26800	53700	54000
Mg	342	330	501	513	619	618	730	729	826	842	1070	1080
Na	73	81	665	700	835	832	638	650	766	767	1080	1130
Cl	167	139	20600	20200	31400	31300	40500	40700	50100	50100	102000	102000
SO_3	371	786	108	318	109	296	93	263	183	370	68	168
SO_4	2110	2450	881	1290	828	1160	900	1320	829	999	386	755
CO_3	542	322	270	218	277	251	288	187	205	120	186	96
$CaSO_4 \cdot 2H_2O$ saturation	50.2	67.7	89.9	131.8	94.1	134.9	116.9	171.0	115.6	139.5	106.3	139.6

Table 5-4. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Forced Oxidation Calcium Chloride Tests

Test	FB-1		FB-3		F5-1		F8-1		F18-1	
Component, ppm	HT	SE	HT	SE	HT	SE	HT	SE	HT	SE
Ca	656	756	563	601	26900	26700	45370	45400	104000	102000
Mg	437	449	523	531	640	652	542	470	409	391
Na	782	811	871	841	603	610	1140	1130	2790	2680
Cl	1	485	127	129	50200	49600	80100	80500	180000	181000
SO_3	4440	4790	21	575	3	390	9	375	2	66
SO_4	183	240	4760	4950	964	1450	671	796	-	-
CO_3	124	125	176	263	7	96	68	128	2	66

When the calcium chloride concentration was increased, the following significant changes in system performance were observed:

- A decrease in system pH
- A decrease in SO_2 removal efficiency
- An increase in calculated gypsum saturation
- An occasional decrease in solids settling rate

Essentially the same trend of chloride ion effects was observed for both natural and forced oxidation conditions. However, the higher percent solids in the filter cake of forced oxidation systems will increase steady state chloride concentrations to much higher levels than in natural oxidation system. This increase tends to counteract the benefits of improved solids quality of forced oxidation over natural oxidation.

5.1.1 Effect of Cl^- on System pH

A comparison of hold tank pH under natural and forced oxidation conditions is shown as a function of chloride concentration in Figure 5-1. The pH decrease in the forced oxidation mode at Cl^- concentrations less than 50,000 ppm was insignificant which confirmed previous data reported by Borgwardt(8). A hold tank pH of 5.2 was obtained at 180,000 ppm Cl^- with forced oxidation, while the same pH drop was observed at only 30,000 ppm Cl^- with natural oxidation. A comparison of natural oxidation hold tank pH data with the theoretical prediction (Equations (4-1) and (4-2) is shown in Figure 5-2. The good agreement confirms that Cl^- affect the system pH as predicted. Two data points obtained previously by Borgwardt(8) are also presented in Figure 5-2 for reference.

5.1.2 Effect of Cl^- on SO_2 Removal

Observed changes in SO_2 removal efficiency as a function of the Cl^- concentration are shown in Figure 5-3. For forced oxidation, the change of SO_2 removal efficiency was insignificant at Cl^- concentrations below 50,000 ppm,

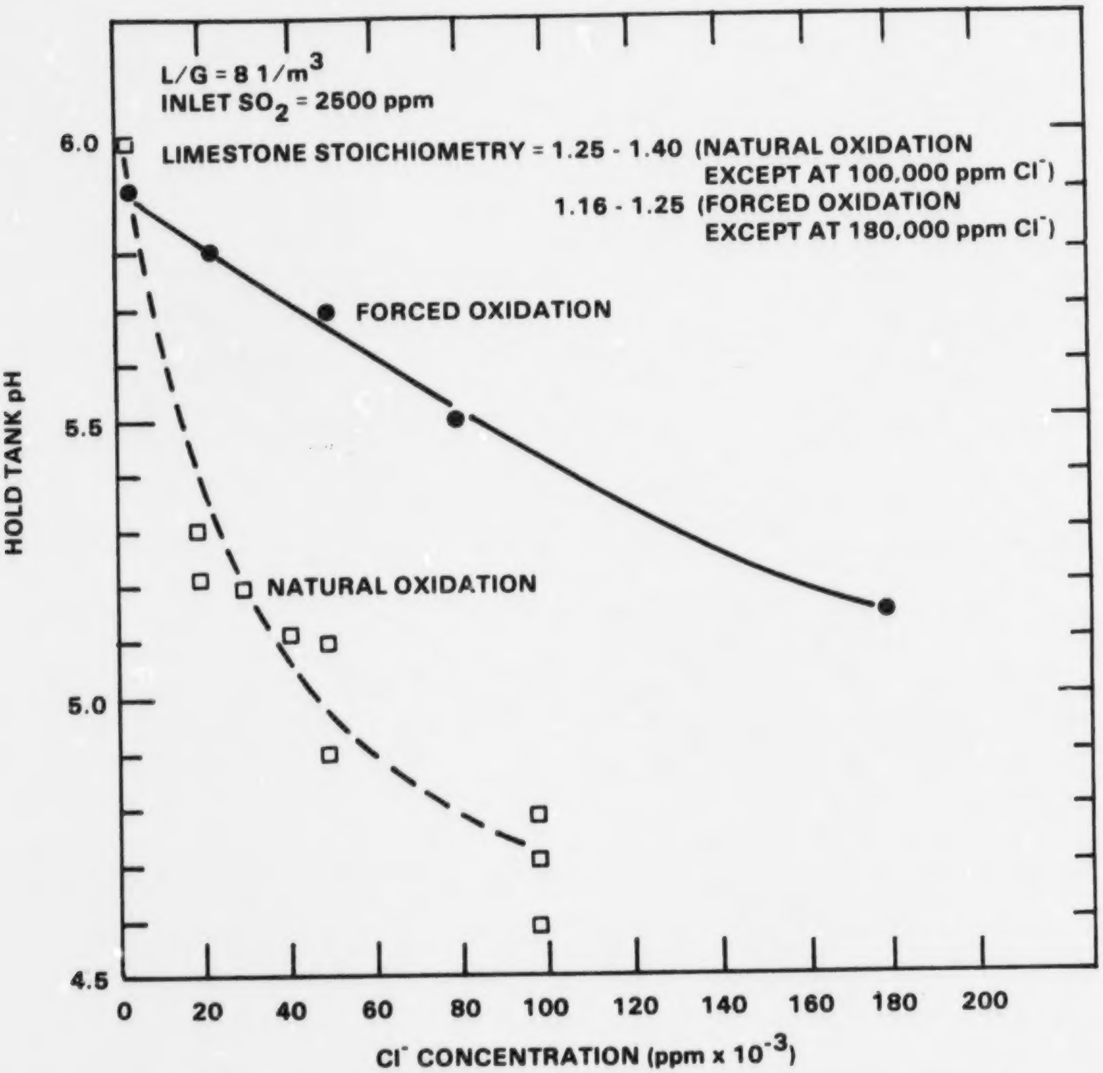


Figure 5-1. Comparison of natural and forced oxidation hold tank pH's of calcium chloride tests.

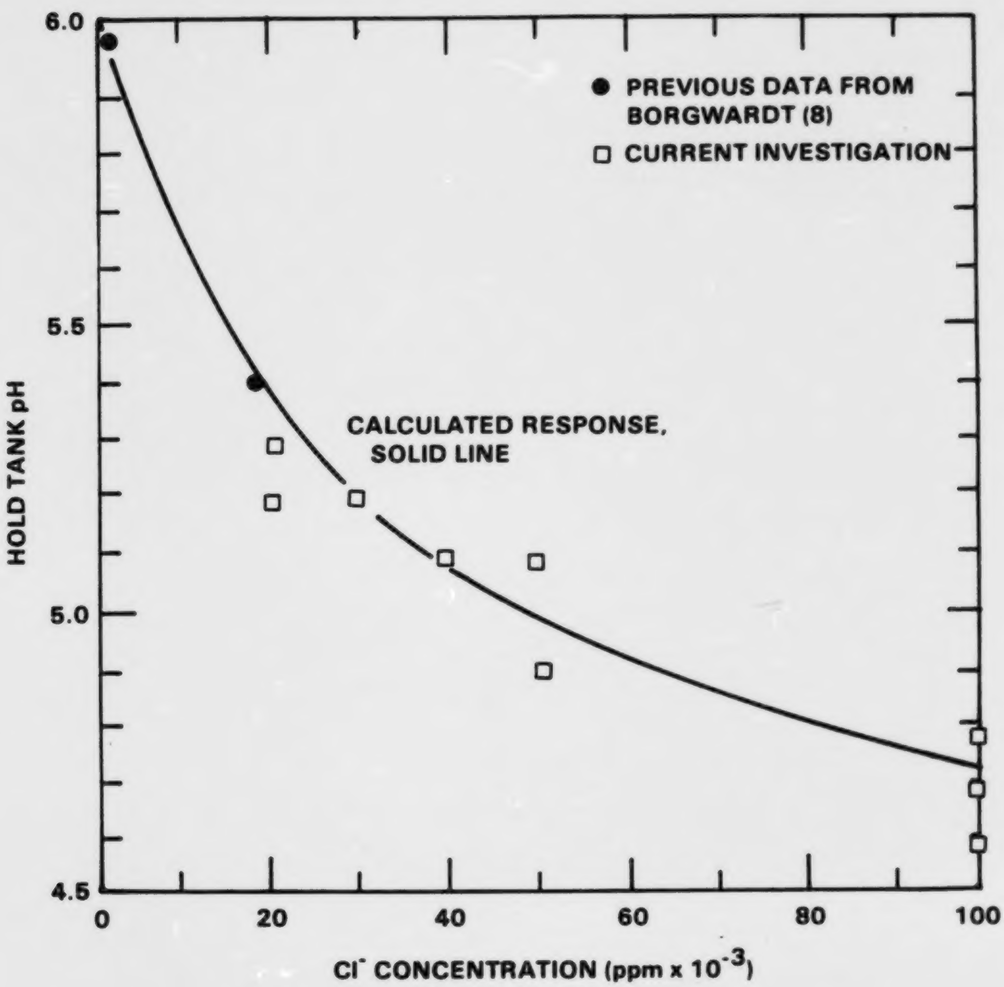


Figure 5-2. Comparison of natural oxidation hold tank pH data of calcium chloride tests with calculated response.

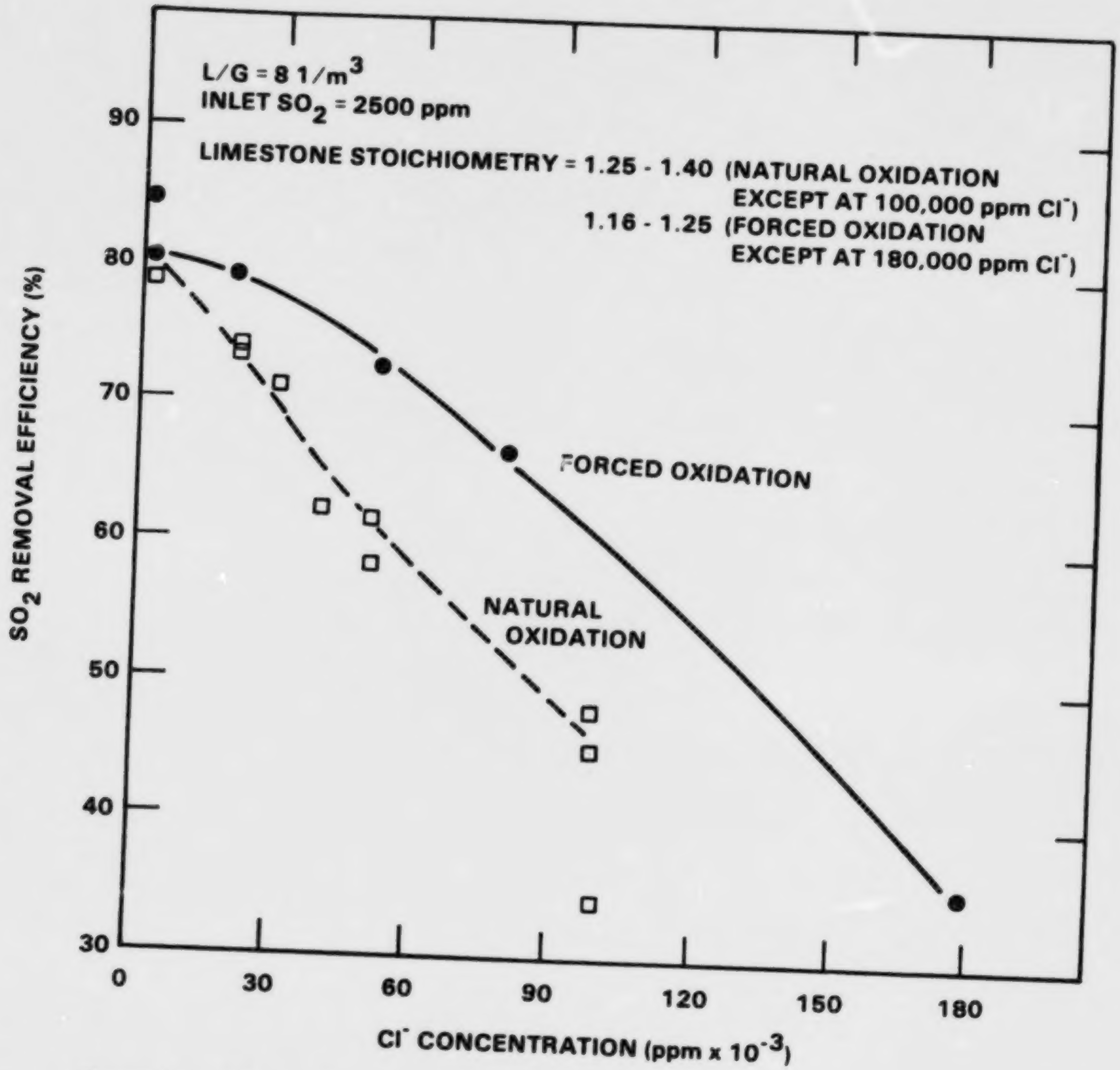


Figure 5-3. Comparison of natural and forced oxidation SO_2 removal efficiencies as a function of slurry chloride concentration for calcium chloride tests.

removal efficiencies (i.e. high and low SO_2 make-per-pass), respectively. Three levels of inlet SO_2 concentration (500, 700 and 2500 ppm) were tested. The purpose of these tests was to broaden the original data base by including potential effects of liquid hold up in the absorber, SO_2 make-per-pass, and the inlet SO_2 concentration which affects the gas-side to liquid-side mass transfer resistance ratio. Results are presented in Table 5-5 for the low limestone stoichiometry and Table 5-6 for low inlet SO_2 concentration tests. Scrubbing liquor ionic species concentration analyses are summarized in Table 5-7.

Since it is difficult to compare tests at different base case conditions, r from equation (4-18) was calculated for each test. Figure 5-4 summarizes the natural and forced oxidation values for r plotted as a function of the chloride ion concentration. When the Cl^- concentration is greater than 20,000 ppm, it is apparent that r has a linear correlation with the chloride concentration and is independent of inlet SO_2 concentration, make-per-pass, liquid holdup in the absorber, and the liquid to gas ratio. This suggests that r is directly correlated with , and the primary effect of chlorides on SO_2 removal is due to changes in gas/solid/liquid equilibria. Figure 5-4 also indicates that the initla base case pH is a significant factor. Tests run with an initial pH of 6.0 (or a limestone stoichiometry of 1.3-1.4) have a significantly steeper slope than the tests run with an initial pH of 5.8-5.9 (or a limestone stoichiometry of 1.15-1.20). Possibly some limestone blinding occurred during the tests with higher limestone stoichiometries (and higher base case pH). Note that the forced oxidation process is not affected by chlorides as severely as the natural oxidation process. This may be due to the lower sulfite concentration at the scrubber inlet and lack of calcium sulfite dissolution in the scrubber.

Table 5-5. Operating Conditions of Low SO_2 Make-Per-Pass and Low Limestone Stoichiometry Calcium Chloride Tests

Test ID	NB-10	N5-LM1	NB-8	N5-HM1	NB-13	N2-4	M5-10
Cl^- concentration, ppm	0.0	50000.0	0.0	50000.0	Basecase	20000	50000
L/G, liters/meter^3	10.7	10.7	11.2	11.2	8.0	8.0	8.0
Absorber feed pH	5.8	4.9	5.8	5.0	5.6	4.9	4.6
Absorber effluent pH	5.4	4.4	5.5	4.5	5.2	4.4	3.9
SO_2 inlet conc., ppm	2500	2510	2450	2520	2520	2540	2530
SO_2 removal efficiency, %	56.0	47.0	89.0	81.0	68.0	65.0	60.0
SO_2 make-per-pass, mmole/liter	4.5	3.9	7.7	6.7	7.09	6.9	6.3
Limestone stoichiometry	1.19	1.11	1.17	1.16	1.16	1.13	1.16
Solids settling rate, cm/min	0.6	0.6	0.6	0.5	0.6	0.5	0.5
Height packing, cm	0.0	0.0	64.8	64.8	38.1	38.1	38.1
Flue gas O_2, %	10.7	11.0	10.9	11.2	6.2	6.6	6.8
Oxidation, %	15.6	30.0	16.3	12.5	11.7	-	11.3
Filter cake solids conc., %	60.8	69.4	61.6	59.3	53.0	52.0	52.0

Table 5-6. Operating Conditions of Low Sulfur Coal Calcium Chloride Tests

Test ID	NB-9	N5-HM3	NB-11	N5-LM3	NB-14	N2-HM1	H5-HM5
Cl^- concentration, ppm	Basecase	50000	Basecase	50000	Basecase	20000	50000
L/G, liters/meter^3	7.2	7.2	4.5	4.7	4.0	4.0	4.0
Absorber feed pH	5.9	5.1	5.9	5.4	5.4	5.2	5.0
Absorber effluent pH	5.5	4.7	5.5	5.1	4.7	4.3	4.1
SO_2 inlet conc., ppm	480	510	490	520	720	730	720
SO_2 removal efficiency, %	92.0	84.0	52.0	43.0	77.0	75.0	68.0
SO_2 make-per-pass, mmole/liter	2.3	2.1	1.9	1.5	4.5	4.7	4.0
Limestone stoichiometry	1.14	1.20	1.22	1.25	1.11	1.07	1.13
Solids settling rate, cm/min	0.6	0.5	0.6	0.5	0.6	0.6	0.6
Height packing, cm	64.8	64.8	0.0	0.0	38.1	38.1	38.1
Flue gas O_2, %	10.1	10.4	10.6	10.8	6.6	6.7	6.8
Oxidation, %	-	19.1	-	32.9	26.5	-	30.5
Filter cake solids conc., %	N/A	83.7	N/A	68.7	62.0	64.0	66.0

Table 5-7. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Composition for Low Sulfur Coal and Low SO_2 Make-Per-Pass Calcium Chloride Tests

Test	NB-9		N5-HM3		NB-10		N5-LM1	
Component, ppm	3/18-19		4/19-23		3/23-24		3/29-4/1	
	HT	SE	HT	SE	HT	SE	HT	SE
Ca	382	388	26700	26500	636	720	26800	26800
Mg	397	386	705	727	541	563	791	818
Na	382	387	484	483	60	65	639	673
Cl	468	448	50600	50700	461	473	50800	50700
SO_3	178	307	111	190	382	865	128	322
SO_4	2940	3210	881	1100	3140	3390	935	1390
CO_3	126	68	136	61	202	128	208	128
$CaSO_4 \cdot 2H_2O$ saturation	58.8	63.5	125.8	157.2	88.6	100.8	131.5	195.8

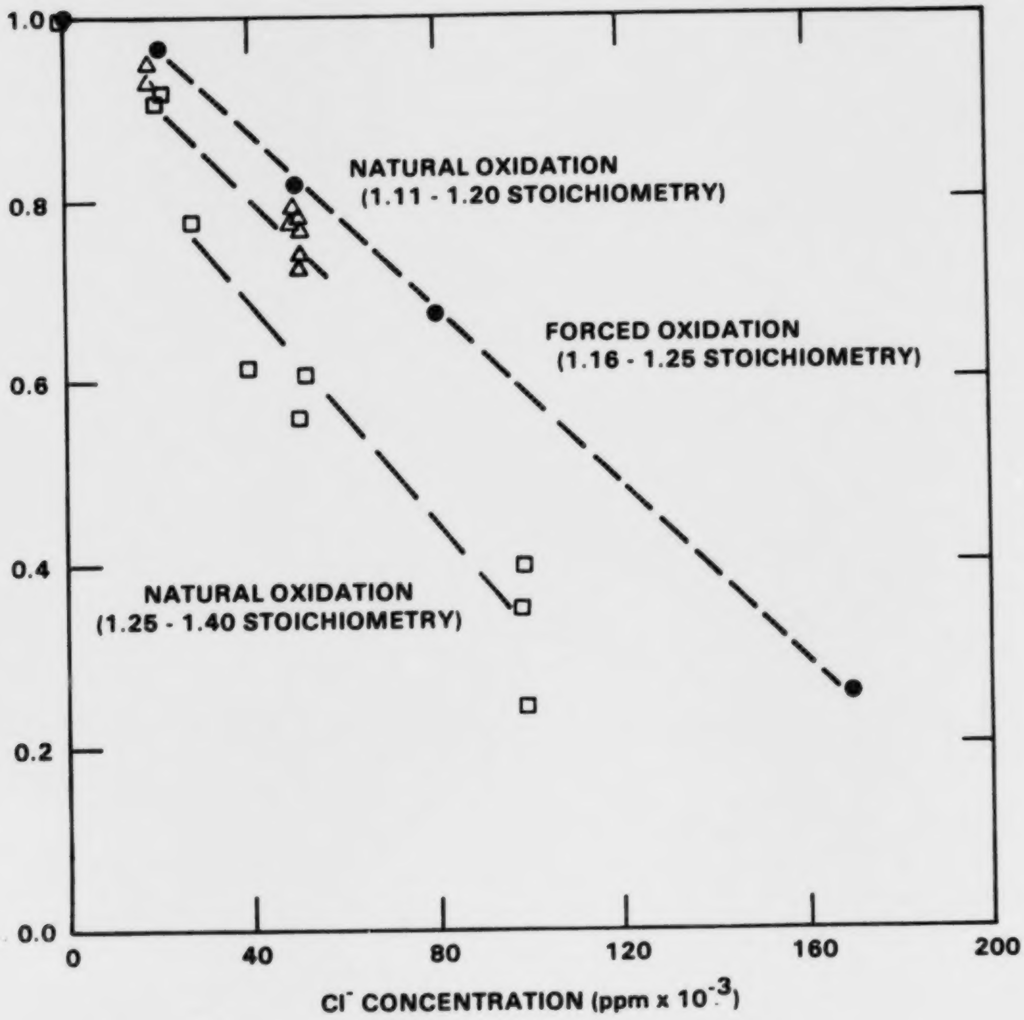


Figure 5-4. r vs. chloride concentration for calcium chloride tests.

which was in accordance with the theoretically predicted Cl^- effect (or lack of effect) on the hold tank pH. The drop of SO_2 removal efficiency under natural oxidation, accompanied by a decrease of hold tank pH, reflects the reduction of dissolved alkalinity by Ca^{2+} and Cl^- accumulation as discussed in the theoretical analysis (Section 4). At the same Cl^- level, a higher SO_2 removal efficiency was always obtained with forced oxidation. But the difference between forced and natural oxidation data can not be fully explained by the effect of the hydrolysis reaction. Other factors related to the mass transfer rate, such as limestone dissolution and calcium sulfite saturation level should also be considered in interpreting the data.

In one natural oxidation test (N10-1), the flue gas HCl injection was stopped for eight hours in order to evaluate the effect of gas phase HCl concentration on scrubber performance at 100,000 ppm Cl^-. No significant changes in hold tank pH were observed but the SO_2 removal efficiency increased by about 4 percentage points which is attributable to the decrease in total acidic gas concentration. Compared with the drop of SO_2 removal efficiency from the base case (more than 30 percentage points), the change caused by gas phase HCl concentration is insignificant. The data confirms that liquid phase calcium chloride accumulation is the major direct cause of decreased SO_2 removal efficiency.

It should be noted that at extremely high Cl^- concentrations, F18-1 at 180,000 ppm with forced oxidation and N10-1 at 100,000 ppm with natural oxidation, phenomena similar to "limestone blinding" were observed. Extremely high limestone stoichiometry (greater than 1.6) was required to maintain reasonable hold tank pH, and SO_2 removal efficiency lower than expected was observed. Data from those two runs should be utilized cautiously.

In addition to these tests, two test series were run at a lower limestone stoichiometry. The two test series had very high and very low base case SO_2

5.1.3 Effect of Cl^- on Gypsum Scaling Potential

By measuring concentrations of major chemical species such as calcium, sulfite, sulfate, magnesium, sodium and chloride in slurry samples taken from the hold tank and scrubber effluent, the calcium sulfate relative saturation level was estimated using the Bechtel Modified Radian equilibrium computer program. Data shown in Figure 5-5 indicate that subsaturated operation is not sustained at high Cl^- concentrations. At Cl^- concentrations greater than 20,000 ppm, the calcium sulfate relative saturation in the hold tank fluctuated near 100 percent and the saturated operation mode prevailed. Solids analysis indicated that a constant level of oxidation was maintained (between 10 and 15 percent) regardless of the Cl^- concentration for most runs. This agrees with the previous analysis that high calcium chloride concentrations may increase the gypsum relative saturation ratio and force the limestone scrubber into a saturated operation mode. The data shown in Figure 5-6 indicate that the calcium sulfate saturation level was always higher than 130 percent in the scrubber effluent and the gypsum scaling potential was considerably higher with increased chloride concentrations. However, no serious scaling was observed in the pilot plant, possibly due to the short term nature of the tests.

5.1.4 Effect of Cl^- on the Solid Settling Rate

The settling rate reported is the average (of the initial three minute period) descent rate of the meniscus between clear supernate and the turbid zone of hold tank slurry sample collected in a 100 ml graduated cylinder and observed under quiescent conditions. Very consistent settling rates were observed in all base case tests. However, when the Cl^-concentration increased, the settling rate varied. Figure 5-7 indicates that under natural oxidation conditions more than a 40 percent drop of solid settling rate was observed with an increase in the Cl^- concentration from base case to 20,000 ppm. However, a significant drop of solid

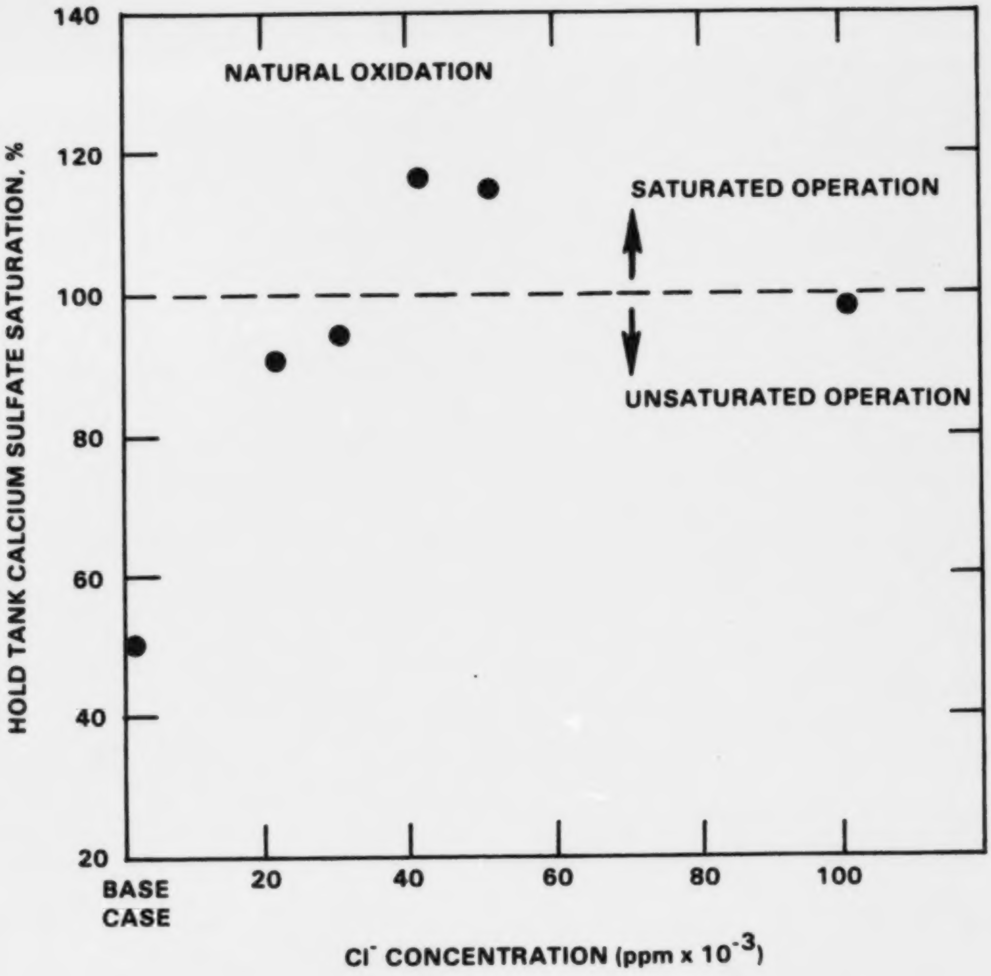


Figure 5-5. Calcium chloride effect on limestone SO_2 scrubber performance: hold tank calcium sulfate saturation vs. Cl^- concentration.

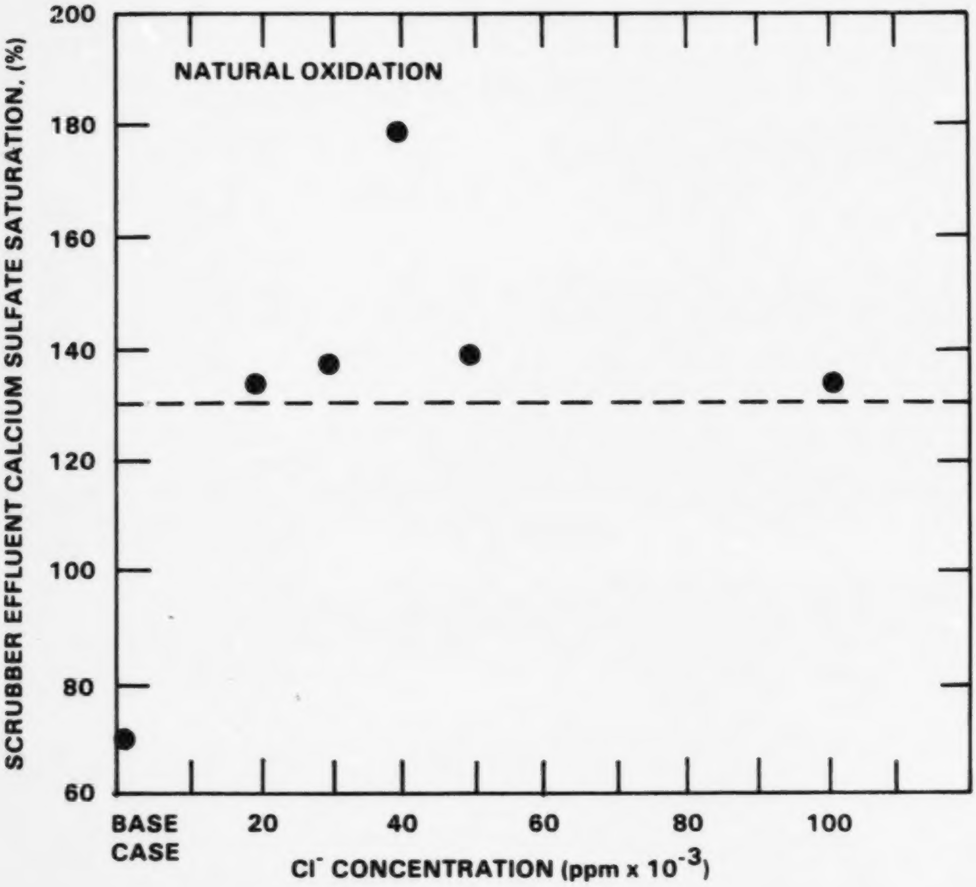
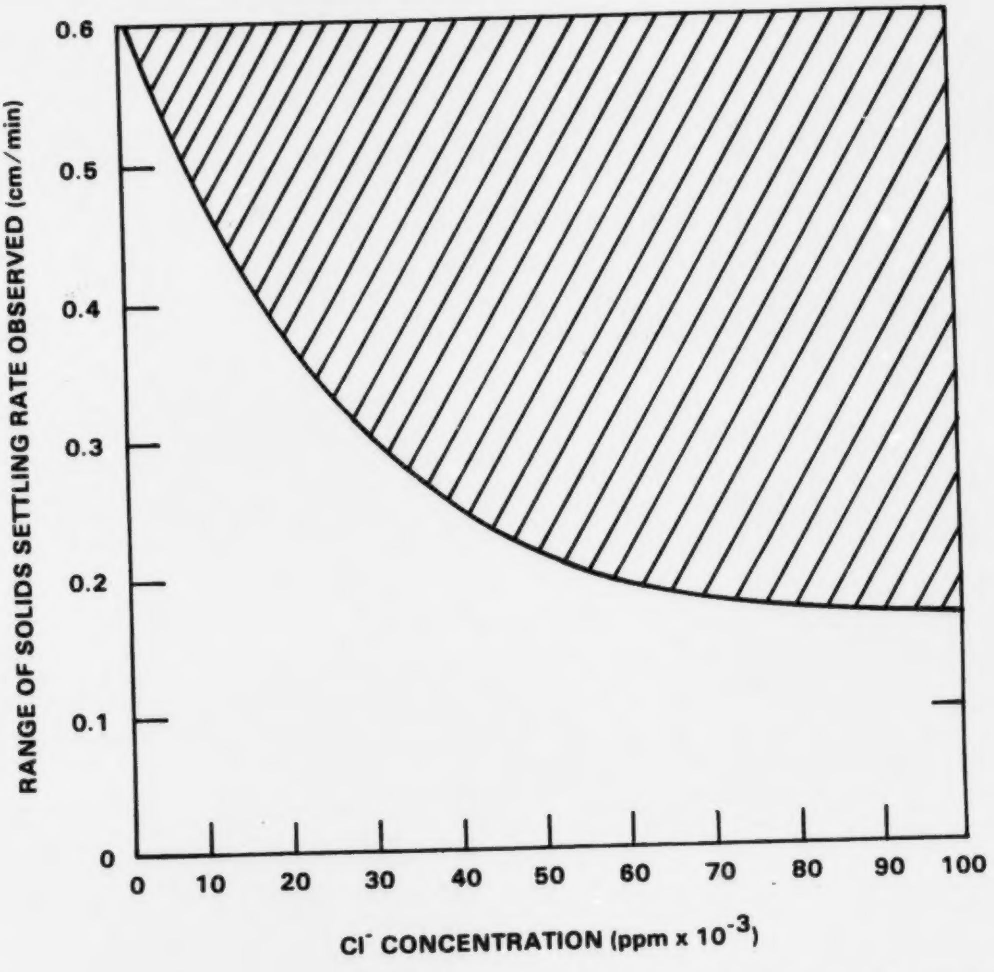


Figure 5-6. Calcium chloride effect on limestone SO_2 scrubber performance: scrubber effluent calcium sulfate saturation vs. Cl^- concentration.



NATURAL OXIDATION
L/G = 8 l/m^3
INLET SO_2 = 2500 ppm
LIMESTONE STOICHIOMETRY = 1.25 - 1.40 (EXCEPT AT 100,000 ppm Cl^-)

Figure 5-7. Calcium chloride effect on natural oxidation limestone SO_2 scrubber performance: solids settling rate observed vs. Cl^- concentration.

settling rate was only occasionally observed during testing. The deterioration of solids settling rate usually occurred as an 8 to 16 hour episode in the middle of a run. Following the poor settling rate episode, the solid settling rate returned to normal. The ranges of settling rate observed under natural oxidation conditions at various Cl^- concentrations are indicated by shaded areas in Figure 5-7. With forced oxidation, as shown in Figure 5-8, no significant change of settling rate was observed (with one exception). During the 180,000 ppm Cl^- forced oxidation test, the settling rate dropped drastically (by one order of magnitude from 4 to 0.9 cm/min) as the chloride concentration increased from 80,000 to 180,000 ppm, but the solids content of the filter cake remained constant.

5.2 EFFECTS OF MAGNESIUM CHLORIDE

5.2.1 Natural Oxidation

The natural oxidation magnesium chloride test consisted of seven runs. Operating conditions for each run are listed in Table 5-8. Scrubbing liquor analyses are summarized in Table 5-9. Results are discussed below.

Significant effects of magnesium chloride on limestone scrubber performance were observed. As shown in Figure 5-9, the accumulation of magnesium chloride actually improved SO_2 removal efficiency when the chloride ion concentration was below 40,000 ppm under natural oxidation conditions. The SO_2 removal efficiency reached 87% at 40,000 ppm Cl^- which was considerably higher than the 80% SO_2 removal at base case (zero chloride addition). However, a significant drop in SO_2 removal efficiency was obtained when the chloride ion concentration was increased beyond 50,000 ppm. At 140,000 ppm Cl^-, only 66.8% SO_2 removal efficiency was obtained.

Another effect observed with magnesium chloride was the drop of hold tank pH. Figure 5-10 indicates that the hold tank pH decreased at a rate similar to that obtained during calcium chloride tests especially at chloride ion

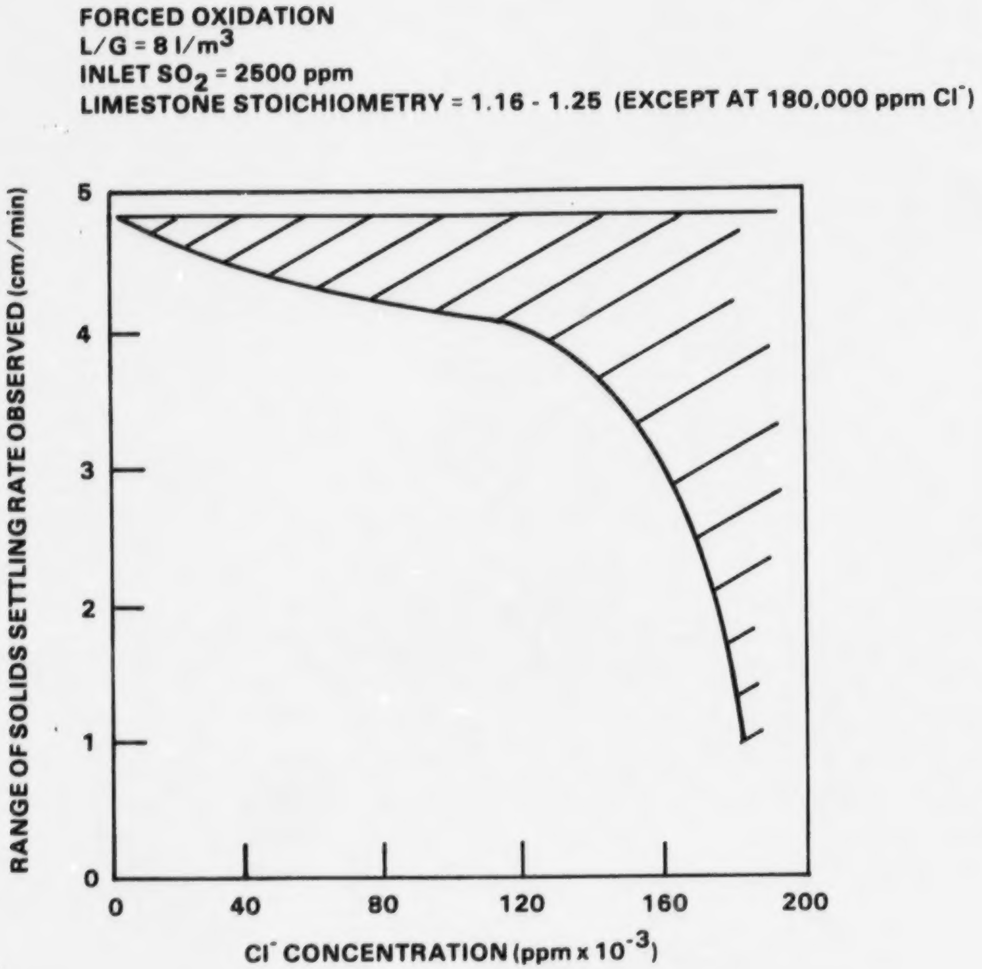


Figure 5-8. Calcium chloride effect on forced oxidation limestone SO_2 scrubber performance: solids settling rate observed vs. Cl^- concentration.

Table 5-8. Operating Conditions for Natural Oxidation Magnesium Chloride Tests

Test	MG-5	MG-6	MG-7	MG-8	MG-12	MG-13	MG-14
Chloride level, ppm	10000	20000	40000	40000	80000	100000	140000
L/G, liter/meter^3	800	8.0	8.0	8.0	8.0	8.0	8.0
Slurry solids, %	10.0	9.6	10.1	10.1	9.9	10.2	9.7
Scrubber feed pH	5.6	5.4	5.1	5.1	5.0	4.8	4.7
Scrubber effluent pH	5.3	5.0	4.7	4.8	4.7	4.5	4.4
Inlet SO_2, ppm	2470	2640	2480	2500	2510	2510	2530
SO_2 absorption, %	838	85.1	87.2	80.7	82.0	75.0	66.8
SO_2 make-per-pass, mmole/liter	8.9	8.9	9.3	8.3	8.6	8.0	7.2
Limestone stoichiometry	1.20	1.20	1.20	1.23	1.19	1.22	1.23
Flue gas O_2, %	5.4	5.4	5.0	4.9	5.1	4.6	5.5
Oxidation, %	6.1	7.0	12.6	-	8.8	-	11.3
Filter cake solids, %	70.6	62.7	70.6	65.4	56.8	57.1	56.3

Table 5-9. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analyses for Natural Oxidation Magnesium Chloride Tests

Test	MG-5		MG-6		MG-12		MG-14	
Component, ppm	HT	SE	HT	SE	HT	SE	HT	SE
Ca	870	865	1330	1570	2177	2180	1450	1460
Mg	4250	4300	6960	6900	27900	27900	47200	47300
Na	235	224	255	256	1207	1207	1117	1117
Cl	10800	11000	19600	20400	80500	80700	140000	140000
SO_3	580	1280	940	1810	1110	1660	1420	1790
SO_4	3040	3600	4190	4370	4090	4440	3220	3930
CO_3	292	184	349	209	303	170	304	213
$CaSO_4 \cdot 2H_2O$ saturation	29.5	33.8	36.1	44.4	3.7(a)	4.1(a)	0.2(a)	0.2(a)

(a) Equilibrium program may be unreliable at these conditions.

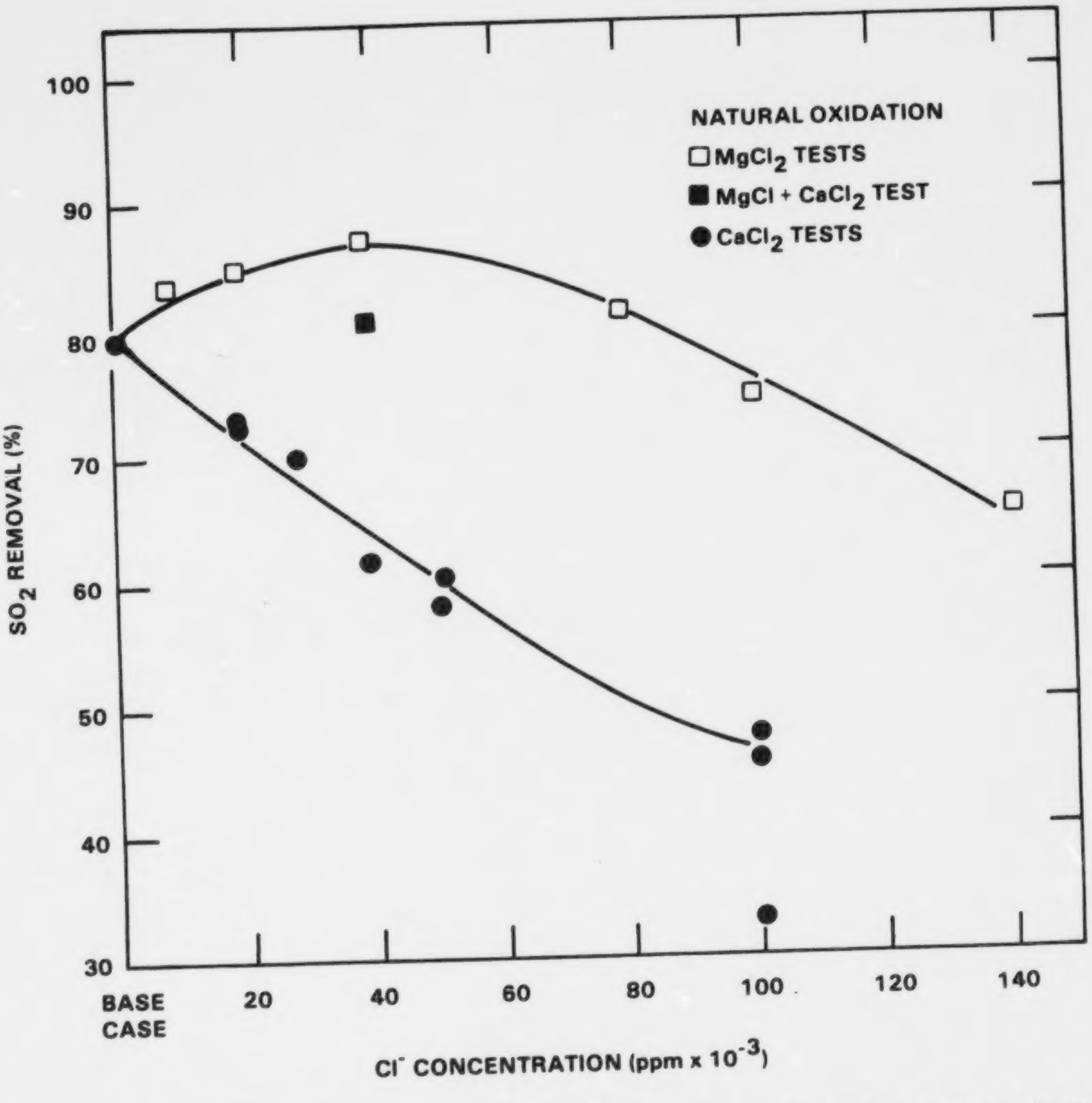


Figure 5-9. Comparison of natural oxidation SO_2 removal efficiencies as a function of slurry chloride concentration.

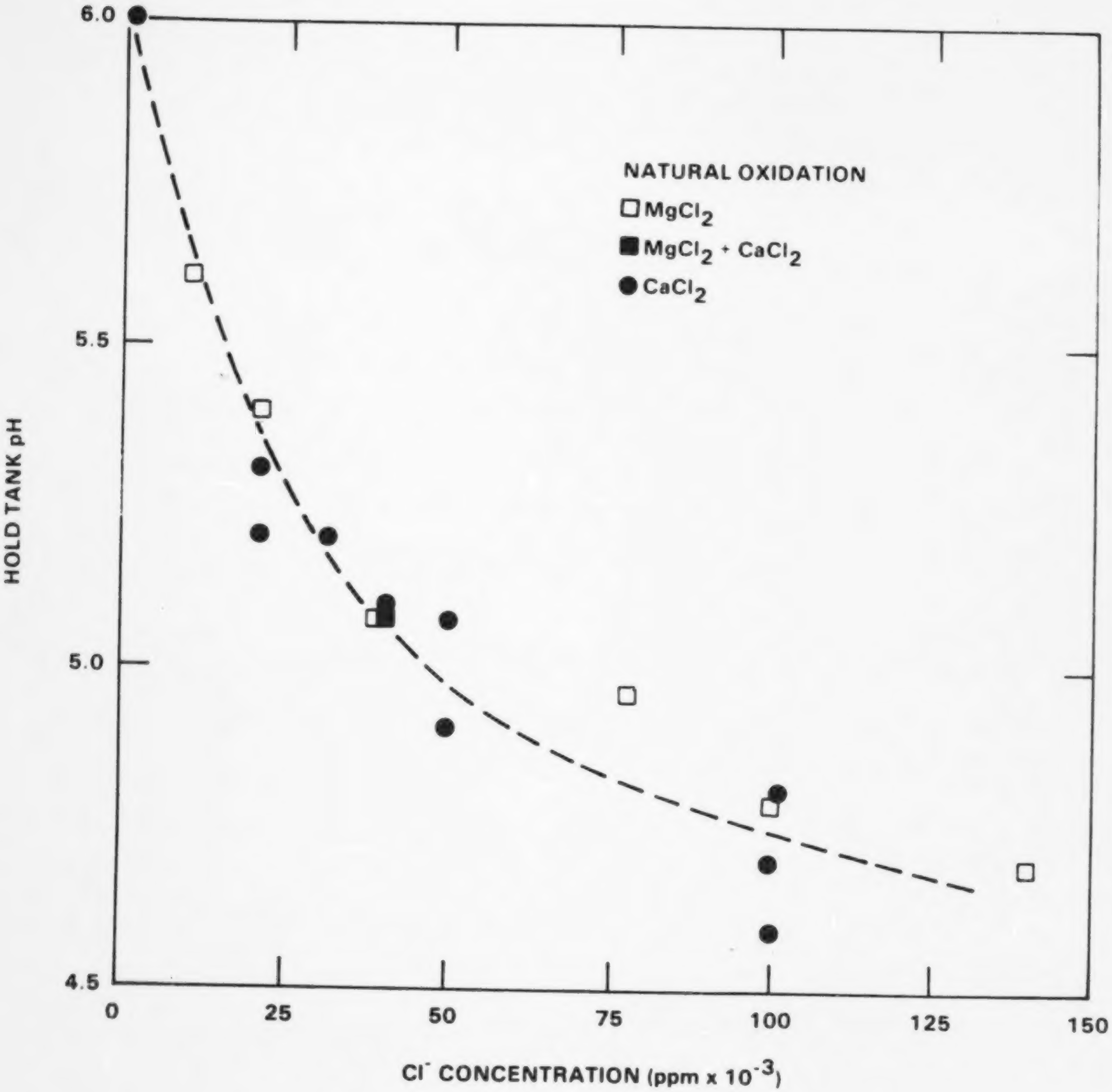


Figure 5-10. Comparison of natural oxidation hold tank pH's as a function of slurry chloride concentration.

concentrations below 50,000 ppm. The hold tank pH data was then plotted against the sum of Ca^{2+} and Mg^{2+} concentrations in Figure 5-11. The hold tank pH's observed during calcium chloride tests agree very well with those obtained from magnesium chloride tests. Figure 5-11 implies that, probably due the similarity in electrical charges, magnesium ions have the same effect as calcium ions in affecting the system pH under natural oxidation conditions. Equation (4-2) can be modified as:

$$[(A_{Ca^{2+}}) + (A_{Mg^{2+}})] = K \frac{A^2_{H^+}}{P_{CO_2}} \tag{5-1}$$

and it is the sum of Ca^{2+} and Mg^{2+} concentrations which acutally determines the system pH values.

One run (MG-8) was made with 50% of the Cl^- associated with Ca^{2+} and 50% with Mg^{2+}. Figures 5-10 and 5-11 indicated that at 40,000 ppm Cl^- (total), similar hold tank pH was obtained with either Ca^{2+}, Mg^{2+} or a combination of Ca^{2+} and Mg^{2+} present in the scrubber. However, a significant difference in SO_2 removal efficiency was observed as shown in Figure 5-9. The SO_2 removal efficiency, which was about the same as the base case level, indicated that the effect of 20,000 ppm Cl^- with Ca^{2+} was offset by 20,000 ppm Cl^- with Mg^{2+}. The results agreed with the observation that magnesium chloride behaved similarly to calcium chloride in reducing the hold tank pH, but had an opposite SO_2 removal efficiency effect at Cl^- concentrations below 40,000 ppm.

Results of chemical analyses of slurry samples at 40,000 ppm Cl^- are listed in Table 5-10. Calcium sulfate saturation levels estimated by the Bechtel modified Radian equilibrium computer program are also shown. As discussed in Section 5-1, a saturation level greater than 100% was obtained with calcium chloride runs. However, only 26% was obtained when 50% of the chloride ion was associated with magnesium. The calcium sulfate saturation level was further

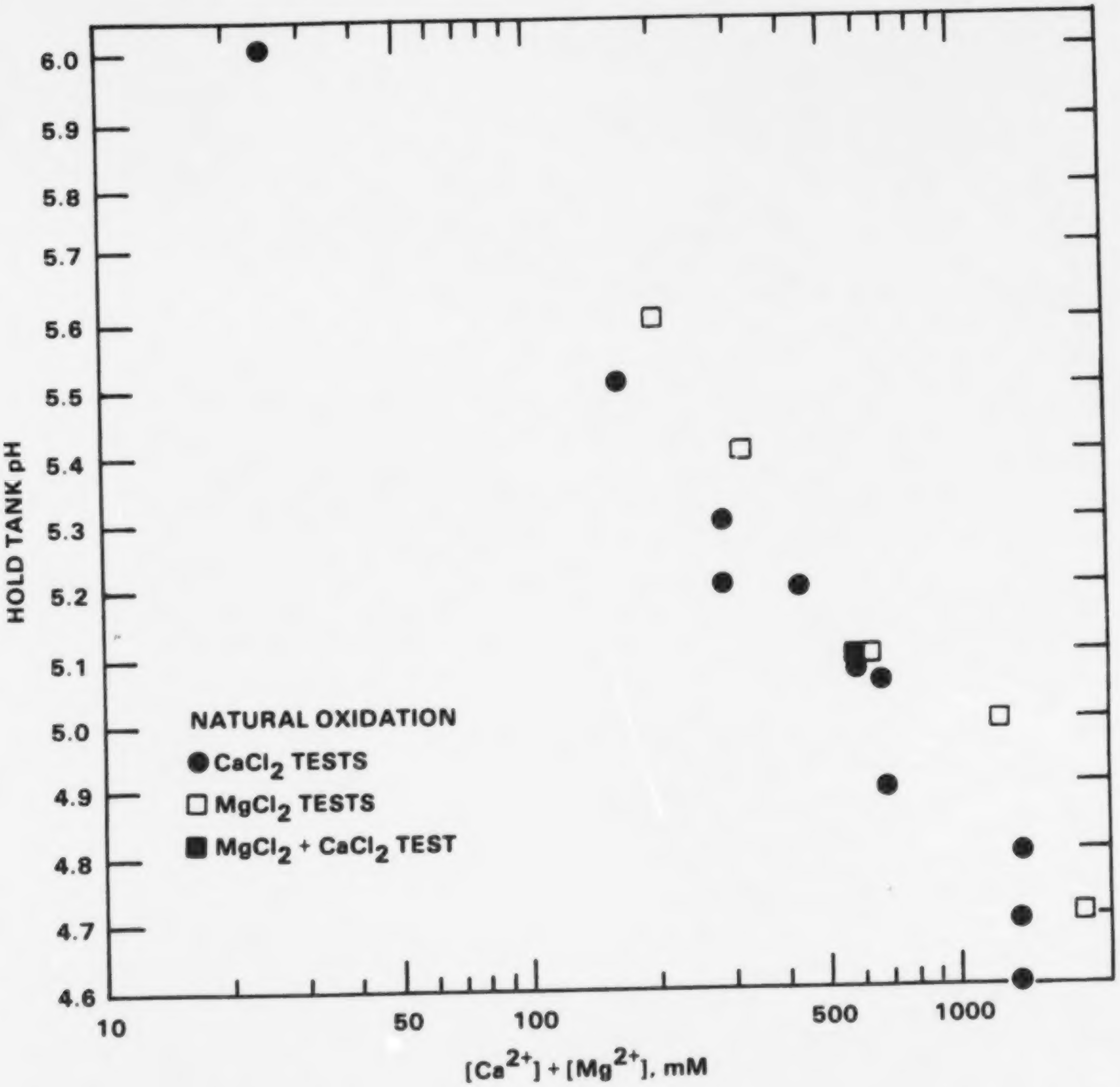


Figure 5-11. Comparison of natural oxidation hold tank pH's as a function of calcium and magnesium ion concentrations.

Table 5-10. Comparison of Calcium Sulfate Saturation Levels Between Calcium and Magnesium Chloride Tests

Test	N4-1		MG-8		MG-7	
Component, ppm	Calcium chloride test		Combination of Calcium and Magnesium Chloride		Magnesium chloride test	
	HT(a)	SE(b)	HT	SE	HT	SE
Ca	22100	21800	10800	10900	1040	1030
Mg	730	729	7010	7020	14100	14100
Na	638	650	590	582	328	343
SO_3	93	263	128	318	1530	2340
SO_4	900	1320	654	666	4200	4680
CO_3	288	187	254	195	333	153
Cl	40500	40700	40400	40400	40800	40600
pH	5.1	4.7	5.1	4.8	5.1	4.7
$CaSO_4 \cdot 2H_2O$ saturation	116.9	171.0	25.9	26.5	10.9(c)	12.5(c)

(a) Hold tank samples
(b) Scrubber effluent samples
(c) Equilibrium program may be unreliable at these conditions

reduced to 11% when magnesium chloride dominated the system. The data indicates that the presence of magnesium apparently reduced the calcium sulfate saturation level and avoided an increased scaling potential.

5.2.2 Forced Oxidation

Five runs were made to evaluate the magnesium chloride effects under forced oxidation conditions. The operating conditions for each run are listed in Table 5-11. The summary of scrubbing liquor analysis is shown in Table 5-12. Results are discussed below.

No significant effect of magnesium chloride on SO_2 removal efficiency was observed at Cl^- concentrations below 70,000 ppm. A slight drop of SO_2 removal efficiency was obtained when the Cl^- concentration was increased to 70,000 ppm as shown in Figure 5-12. At 150,000 ppm Cl^-, the SO_2 removal efficiency reached 68% which was 12 percentage points less than the base case. Figure 5-13 shows that a significant drop of hold tank pH was observed with the accumulation of magnesium chloride. The hold tank pH decreased from 5.9 for the base case to 5.6 at 70,000 ppm Cl^- and to 5.4 at 110,000 ppm Cl^-. Figure 5-13 also indicates that the hold tank pH dropped at a rate similar to that observed during previous calcium chloride tests.

One run (MG-11) was made with 50% of the chloride associated with calcium and 50% with magnesium. Figures 5-12 and 5-13 indicate that at 110,000 ppm chloride (total) similar hold tank pH was obtained with either Ca^{2+}, Mg^{2+} or a combination of Ca^{2+} and Mg^{2+} present in the scrubber. However, a significant difference in SO_2 removal efficiency was observed. It was concluded that when the Cl^- concentration was lower than 70,000 ppm, SO_2 removal efficiency was not significantly affected by the presence of chloride associated with magnesium. Yet, the SO_2 removal efficiency was decreased by chloride when calcium was present. As calcium increased, SO_2 removal efficiency decreased.

Table 5-11. Operating Conditions for Forced Oxidation Magnesium Chloride Tests

Test	MG-9	MG-10	MG-11	MG-15	MG-16
Chloride level, ppm	70000	110000	110000	40000	150000
L/G, liter/meter^3	8.0	8.0	8.0	8.0	8.0
Slurry solids, %	11.2	10.1	10.6	10.1	9.6
Scrubber feed pH	5.6	5.4	5.3	5.8	5.4
Scrubber effluent pH	4.5	4.3	4.2	4.8	4.3
Inlet SO_2, ppm	2470	2520	2520	2470	2470
SO_2 absorption, %	81.6	76.5	70.2	82.1	67.7
SO_2 make-per-pass,	8.3	7.8	7.3	8.5	6.9
Limestone stoichiometry	1.24	1.25	1.25	1.27	1.27
Flue gas O_2, %	8.6	8.7	6.2	5.6	5.7
Oxidation, %	93.5	-	98.4	-	97.4
Filter cake solids, %	83.5	82.5	81.5	81.5	83.0

Table 5-12. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Forced Oxidation Magnesium Chloride Tests

Test	MG-9		MG-10		MG-11		MG-16	
Component, ppm	HT	SE	HT	SE	HT	SE	HT	SE
Ca	3230	3270	2790	2870	31000	31100	2330	2330
Mg	23200	23300	34600	36200	18200	118000	51300	51400
Na	1580	1560	1420	1410	2210	2150	1350	1340
Cl	70200	70200	111000	111000	112000	112000	147000	147000
SO_3	7.1	448	12	487	11	447	21	328
SO_4	6880	7180	6790	7420	856	882	6790	6990
CO_3	44	99	78	112	340	99	120	85

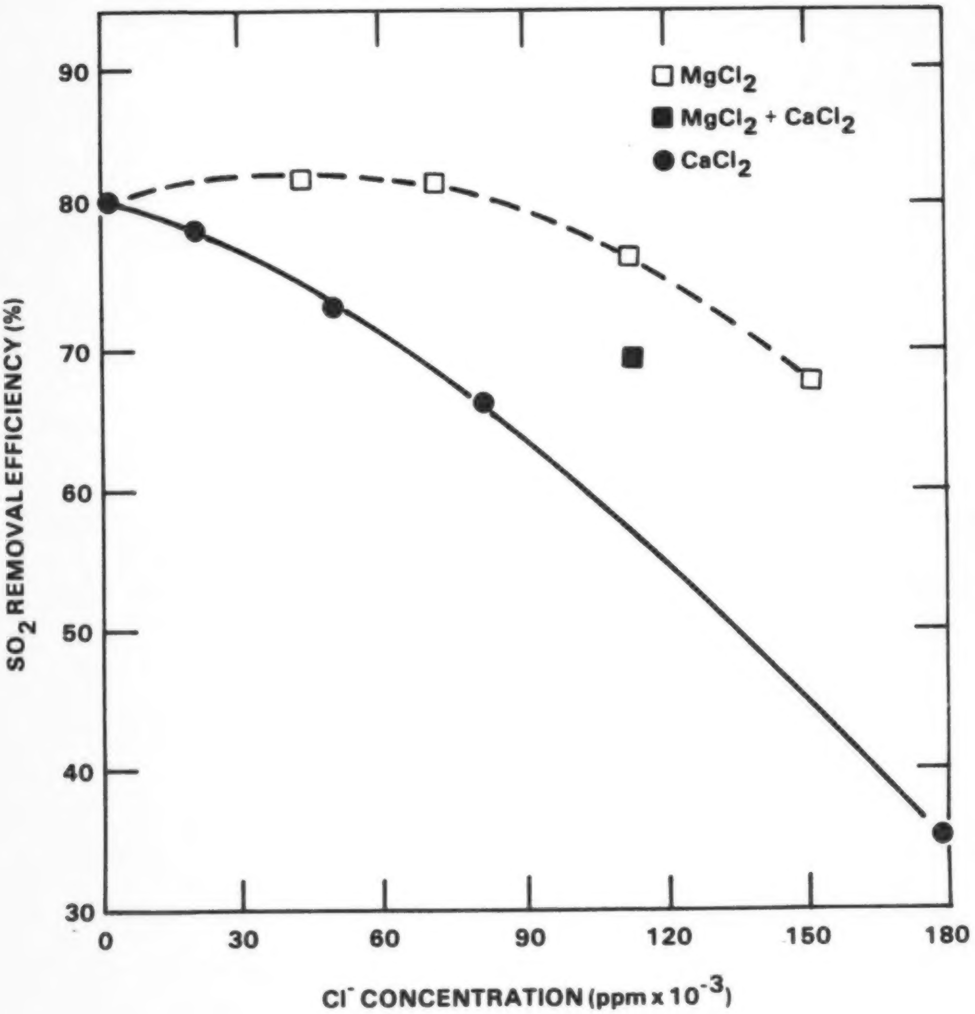


Figure 5-12. Comparison of forced oxidation SO_2 removal efficiencies as a function of slurry chloride concentration.

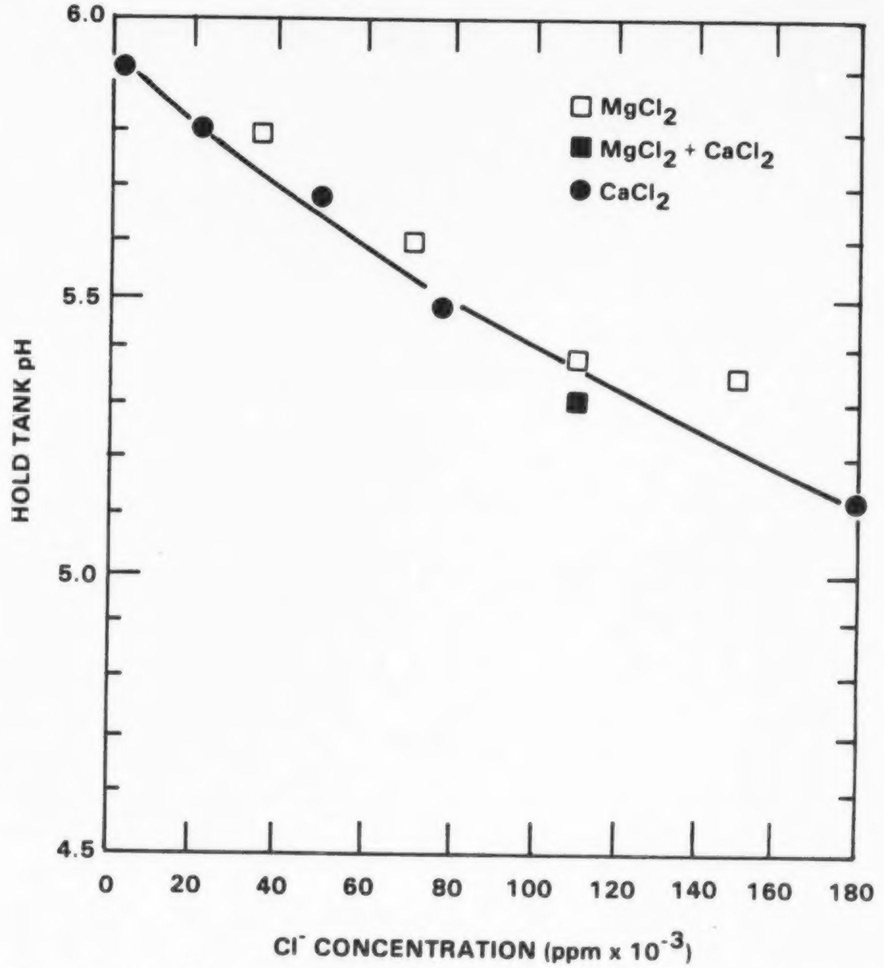


Figure 5-13. Comparison of forced oxidation hold tank pH's as a function of slurry chloride concentration.

5.3 EFFECTS OF SODIUM CHLORIDE

5.3.1 Natural Oxidation

Five runs were made to evaluate the sodium chloride effects under natural oxidation conditions. Operating conditions of each run are listed in Table 5-13. Results shown in Figures 5-14 and 5-15 indicate that no significant effects were observed with the accumulation of sodium chloride until the Cl^- concentration reached 50,000 ppm. However, when the Cl^- concentration exceeded 50,000 ppm, significant drops in both SO_2 removal efficiency and hold tank pH were obtained. At 110,000 ppm Cl^-, 61.5% SO_2 removal efficiency was obtained which was considerably lower than the base case efficiency (80%). The hold tank pH was 5.4 which was also significantly lower than the base case pH of 6.0. Results of chemical analyses of slurry samples are listed in Table 5-14. The relative calcium sulfate saturation levels estimated by the Bechtel modified Radian Equilibrium computer program indicated that an unsaturated operation mode was sustained throughout the system.

One run (NN-2) was made at a 50,000 ppm Cl^- concentration with 50% of the Cl^- associated with Na^+ and 50% with Ca^{2+}. Figures 5-14 and 5-15 indicate that both the SO_2 removal efficiency and hold tank pH were between the data obtained with only sodium chloride or calcium chloride. Significantly higher scaling potential resulted as the calcium sulfate saturation level in the scrubber effluent increased to 169.4% as shown in Table 5-14.

The hold tank pH data was plotted against the sum of Ca^{2+} and Mg^{2+} concentrations in Figure 5-16. Figure 5-16 indicates that the pH values observed during sodium chloride tests agree with those obtained from calcium and magnesium chloride runs. Figure 5-16 confirms that the hold tank pH was determined by the sum of Ca^{2+} and Mg^{2+} concentrations. Comparison of Figures 5-15 and 5-16 indicates that sodium ion does not affect the system pH.

Table 5-13. Operating Conditions for Natural Oxidation Sodium Chloride Tests

Test	NN-1	NN-2	NN-3	NN-4	NN-5
Chloride level, ppm	25000	50000	50000	110000	80000
L/G, liter/meter^3	8.0	8.0	8.0	8.0	8.0
Slurry solids, %	9.4	9.6	9.7	9.4	9.6
Scrubber feed pH	5.9	5.2	5.9	5.4	5.6
Scrubber effluent pH	5.5	4.8	5.6	5.1	5.2
Inlet SO_2, ppm	2500	2510	2480	2550	2500
SO_2 absorption, %	79	72	79	62	71
SO_2 make-per-pass,	8.4	7.6	8.8	6.3	7.1
Limestone stoichiometry	1.39	1.43	1.34	1.33	1.33
Flue gas O_2, %	10.3	10.5	10.6	5.5	5.5
Oxidation, %	22	22	16.4	-	8.7
Filter cake solids, %	57	59	59	51	53

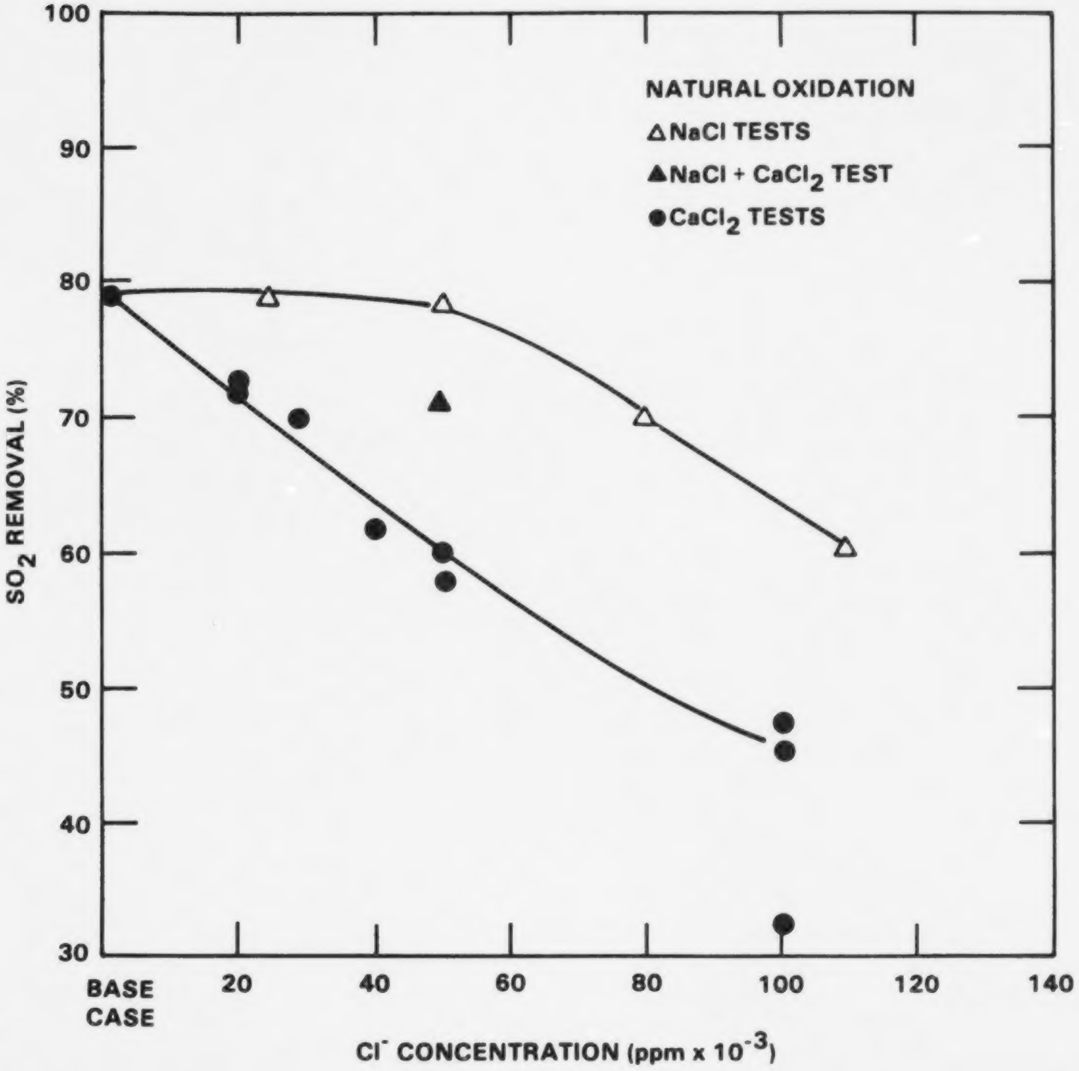


Figure 5-14. Comparison of natural oxidation SO$_2$ removal efficiencies as a function of slurry chloride concentration.

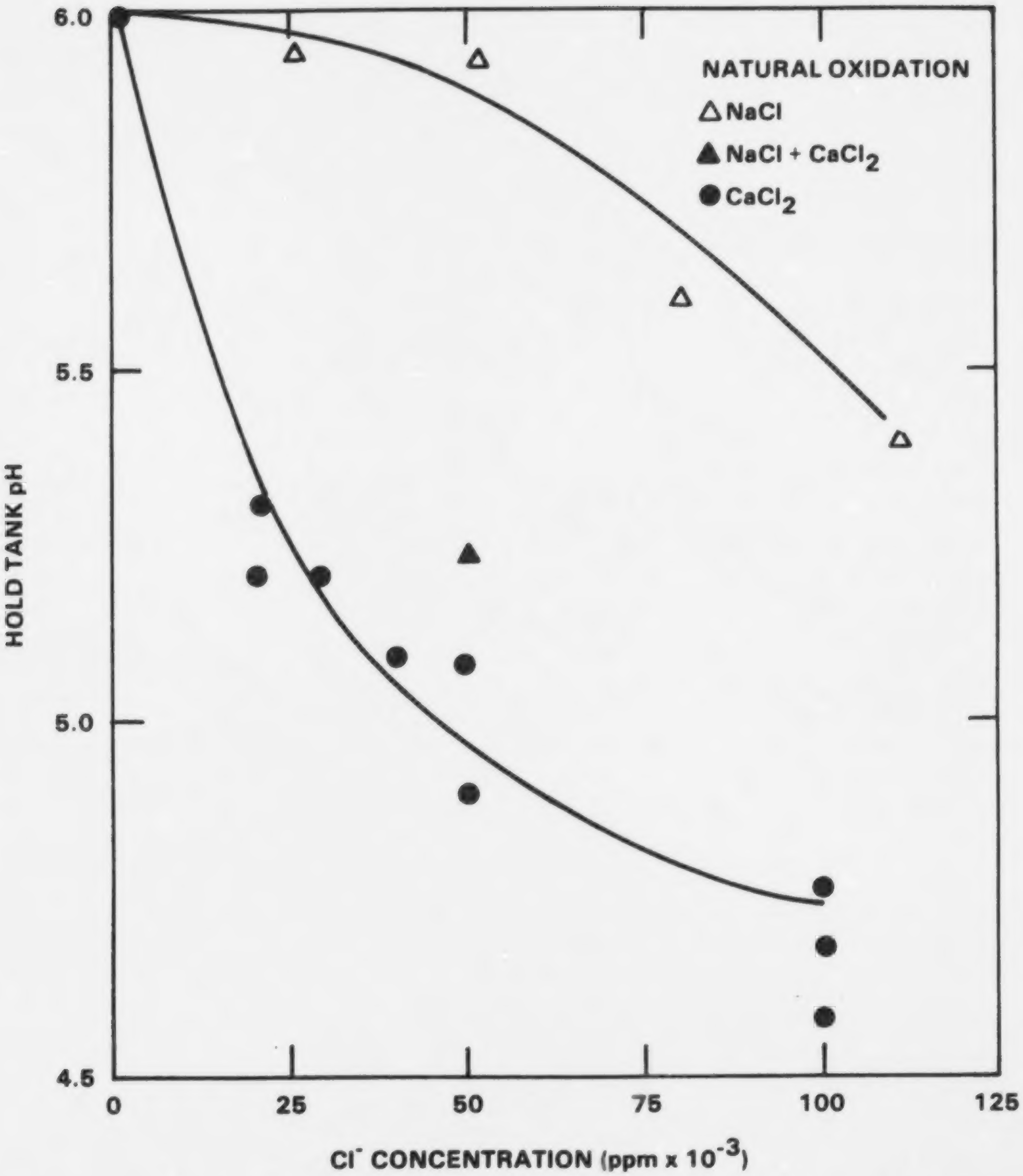


Figure 5-15. Comparison of natural oxidation hold tank pH's as a function of slurry chloride concentration.

Table 5-14. Comparison of Calcium Sulfate Saturation Levels for Sodium Chloride Tests

Test	NN-1		NN-5		NN-2	
Component, ppm	(Sodium chloride test at 25,000 Cl^-)		(Sodium chloride test at 80,000 Cl^-)		(Combination of calcium and sodium chloride)	
	HT	SE	HT	SE	HT	SE
Ca	932	1010	3770	3780	13800	14100
Mg	183	188	437	439	234	244
Na	16300	16300	51000	51100	16700	16600
SO_3	428	949	262	838	194	421
SO_4	2020	2100	1740	1910	1180	1610
CO_3	541	327	221	137	237	149
Cl	25700	25400	80200	80100	50100	50200
pH	5.9	5.5	5.6	5.2	5.2	4.8
$CaSO_4 \cdot 2H_2O$ saturation, %	27.4	30.5	60.6	66.2	124.1	169.4

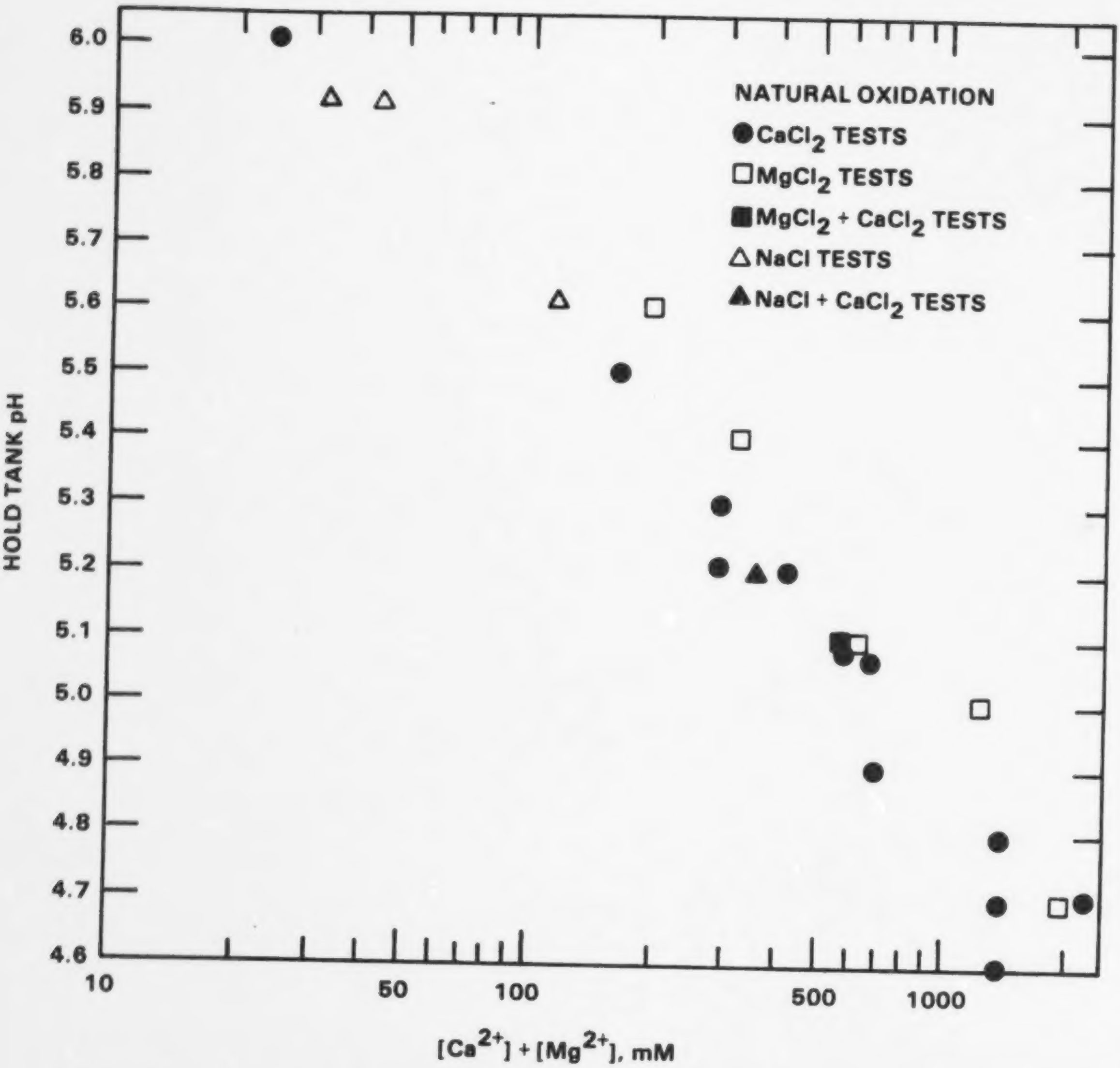


Figure 5-16. Comparison of natural oxidation hold tank pH's as a function of calcium and magnesium ion concentrations.

5.3.2 Forced Oxidation

Six runs were made to evaluate the sodium chloride effects under forced oxidation conditions. Operating conditions of each run are listed in Table 5-15. Summaries of scrubbing liquor analysis are shown in Table 5-16. Results shown in Figures 5-17 and 5-18 indicate that the SO_2 removal efficiency and hold tank pH varied, but not significantly, with the accumulation of sodium chloride up to 70,000 ppm Cl^-. The SO_2 removal efficiency increased slightly from 80% (base case) to 82.9% at 30,000 ppm Cl^- and then dropped to 79.1% at 70,000 ppm Cl^-. The hold tank pH also decreased by only about 0.15 units. However, significant drops of SO_2 removal efficiency and hold tank pH were obtained when the Cl^- concentration was above 70,000 ppm. The SO_2 removal efficiency decreased from 76% at 90,000 ppm Cl^- to 70% at 110,000 ppm, and further to 61% at 150,000 ppm. The hold tank pH also dropped from 5.75 to 5.6 and 5.4.

One run (FN-4) was made with 50% of the Cl^- associated with sodium and 50% with calcium. Figures 5-17 and 5-18 indicate that both the SO_2 removal efficiency and hold tank pH observed were between the data obtained with only sodium chloride or calcium chloride.

Table 5-15. Operating Conditions for Forced Oxidation Sodium Chloride Tests

Test	FN-1	FN-2	FN-3	FN-4	FN-5	FN-6
Chloride level, ppm	30000	70000	90000	90000	110000	150000
L/G, liter/meter^3	8.0	8.0	8.0	8.0	8.0	8.0
Slurry solids, %	9.7	11.1	9.7	9.8	9.8	10.1
Scrubber feed pH	5.9	5.75	5.75	5.6	5.6	5.4
Scrubber effluent pH	5.0	4.9	4.9	4.6	4.6	4.4
Inlet SO_2, ppm	2540	2600	2550	2470	2490	2520
SO_2 absorption, %	82.9	79.1	76.6	72.4	70.1	61.0
SO_2 make-per-pass,	8.5	8.0	7.9	7.4	7.4	6.24
Limestone stoichiometry	1.20	1.25	1.25	1.25	1.23	1.25
Flue gas O_2, %	4.6	3.8	4.4	4.2	6.5	3.0
Oxidation, %	100	-	100	-	100	-
Filter cake solids, %	82.5	80.5	82.1	82.1	81.2	79.5

Table 5-16. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Forced Oxidation Sodium Chloride Tests

Test	FN-1		FN-3		FN-5	
Component, ppm	HT	SE	HT	SE	HT	SE
Ca	2290	2340	2460	2560	2460	2400
Mg	521	523	485	499	542	474
Na	20000	20100	58400	58500	72100	71300
Cl	32400	32400	90000	89900	112000	113000
SO_3	8	449	1	445	1	414
SO_4	4540	4510	4770	4830	3880	3670
CO_3	62	127	25	98	26	76

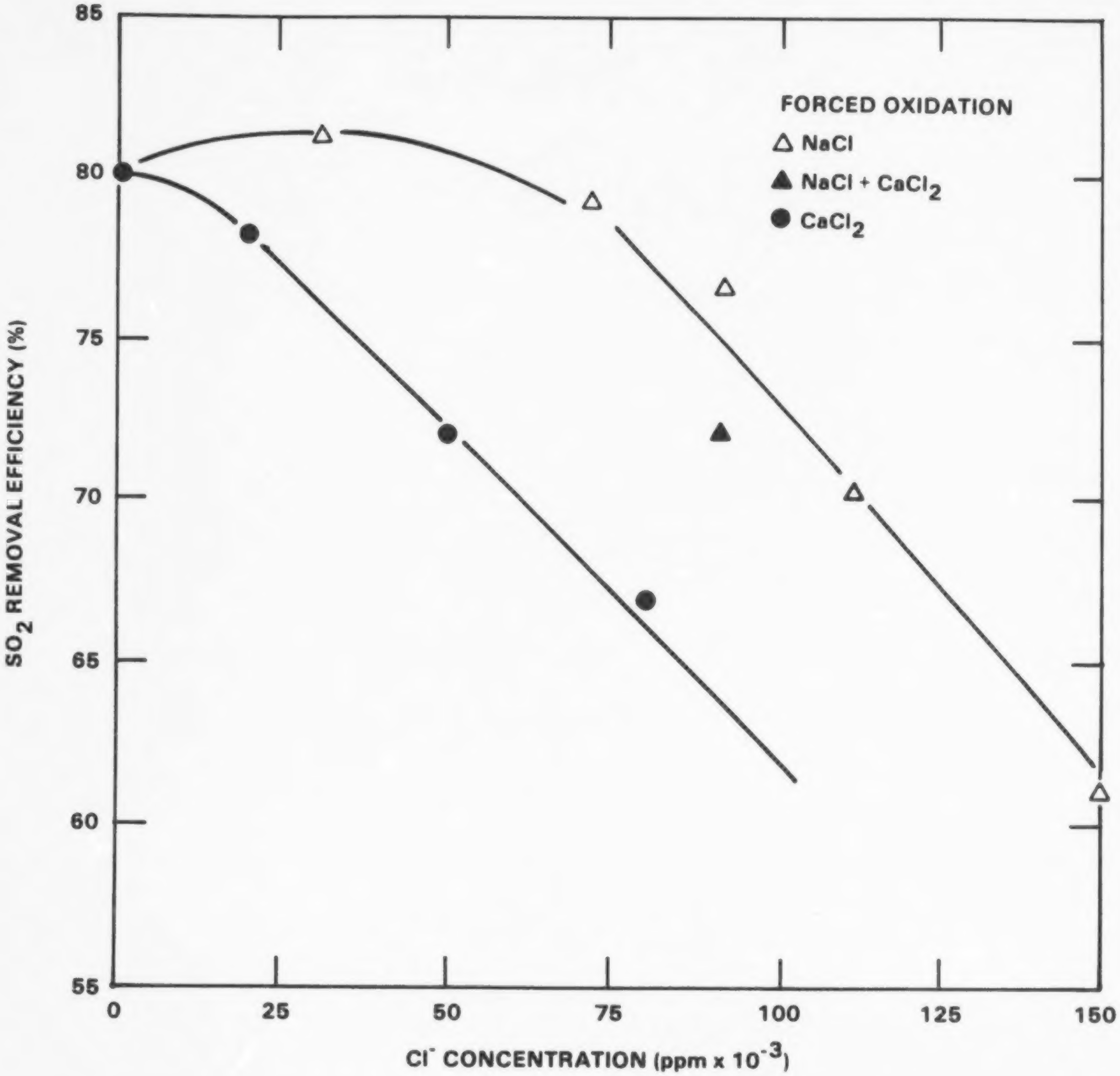


Figure 5-17. Comparison of forced oxidation SO_2 removal efficiencies as a function of slurry chloride concentration.

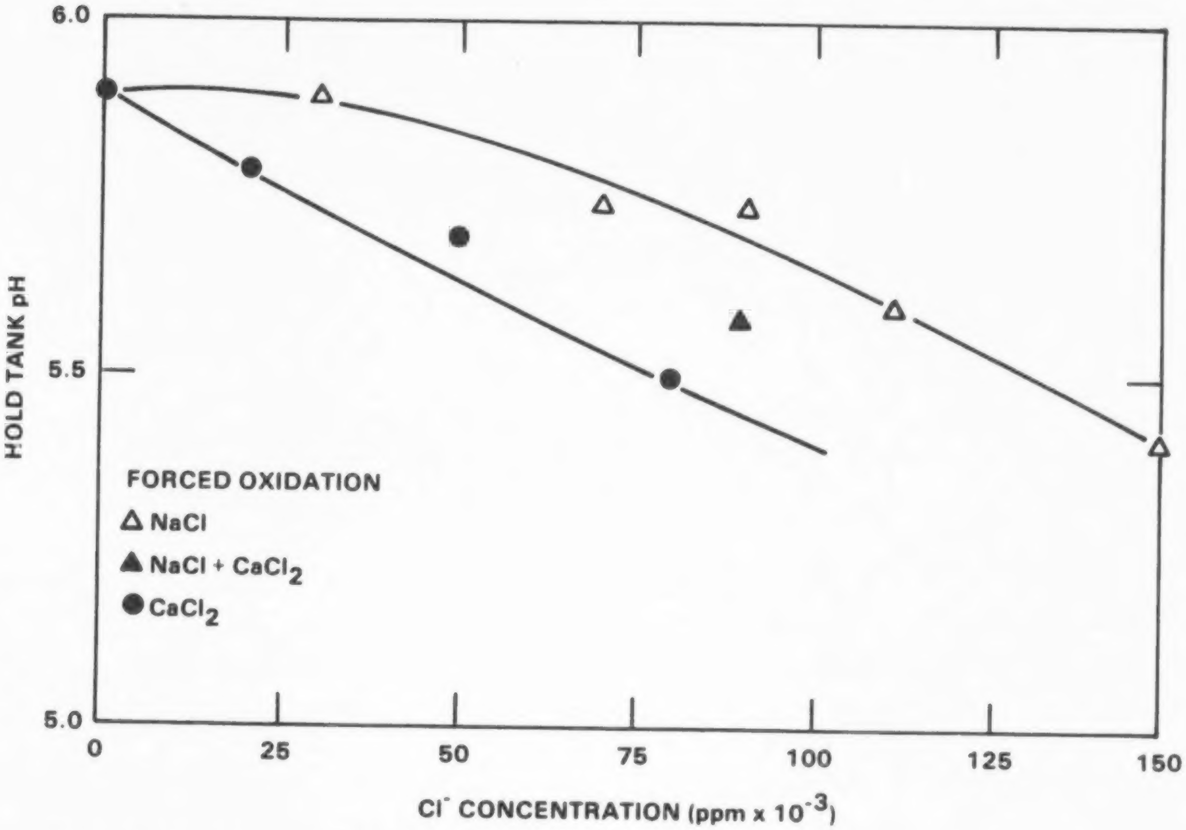


Figure 5-18. Comparison of forced oxidation hold tank pH's as a function of slurry chloride concentration.

SECTION 6

EVALUATION OF CALCIUM CHLORIDE EFFECT COUNTERMEASURES

It was shown in Section 5 that the SO_2 removal efficiency of limestone scrubbing was reduced by the accumulation of chloride ions, especially calcium chloride. In order to counteract the effects of chloride, short term pilot plant tests were conducted in an effort to evaluate process modifications which might offset the observed effect of calcium chloride and thereby raise SO_2 removal efficiency.

Data shown in Section 5 indicated that the most significant effect of Cl^- on SO_2 removal efficiency was observed with natural oxidation at high sulfur coal, high SO_2 make-per-pass conditions and a limestone stoichiometry of 1.35. It was decided that since these were the most sever conditions they should be utilized for process modification evaluation tests.

6.1 HIGH LIMESTONE STOICHIOMETRY TESTS

Short term pilot plant tests were conducted to evaluate the effectiveness of increasing limestone stoichiometry. The operating conditions and test results with high SO_2 make-per-pass (greater than 8 mmole/liter) are shown in Table 6-1. Limestone stoichiometry ratios required to reach the base case SO_2 removal efficiency at various chloride concentrations are plotted in Figure 6-1. Data shown in Figure 6-1 indicate that an extremely high limestone stoichiometry is required to offset the depressed SO_2 removal efficiency. At 40,000 ppm Cl^-, the limestone feedrate had to be increased by about 200 percent to reach the base case SO_2 removal efficiency.

The effectiveness of increasing limestone stoichiometry with low SO_2 make-per-pass (less than 5 mmole/liter) was evaluated with a multigrid scrubber. All the packing spheres were removed from the scrubber which

Table 6-1. Operating Conditions of High Limestone Stoichiometry Calcium Chloride Tests with High SO_2 Make-per-pass

Test	NB-1	N2-2	N3-2	N4-2
Cl^- concentration, ppm	Basecase	20000	30000	40000
L/G ratio, liter/meter^3	8.0	8.0	8.0	8.0
Slurry solids, %	10.1	10.1	9.9	9.8
Scrubber feed pH	6.0	5.4	5.4	5.2
Scrubber effluent pH	5.6	5.2	5.1	5.6
Inlet SO_2, ppm	2670	2570	2570	2670
SO_2 absorption, %	79	80	79	81
SO_2 make-per-pass, mmole/liter	8.4	8.5	8.4	8.4
Limestone stoichiometry	1.25	2.0	2.6	3.0
Height of packing, cm	53.3	53.3	53.3	53.3
Flue gas O_2, %	10.4	10.1	11.2	11.8
Test period, hours	67	10	12	10
Slurry settling rate, cm/min	0.6	0.5	0.6	0.37

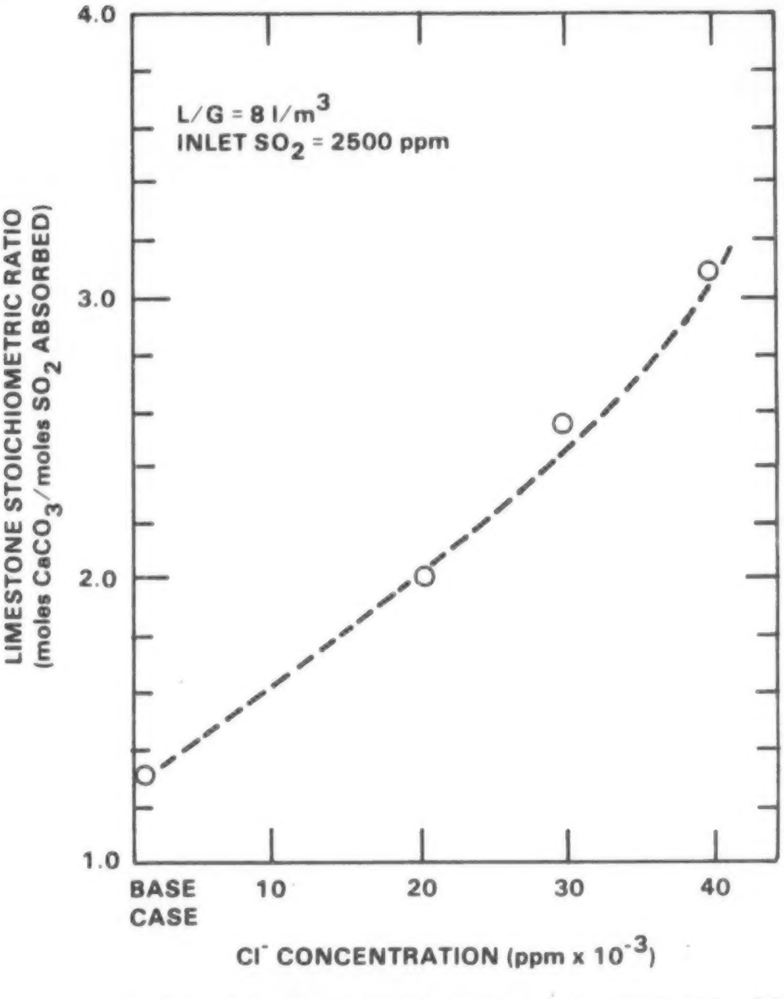


Figure 6-1. Limestone stoichiometric ratio required for 80% SO_2 removal vs. Cl^- concentration with natural oxidation.

resulted in low SO_2 removal efficiency and low SO_2 make-per-pass. The operating conditions and test results are shown in Table 6-2. Comparing the data of runs NB-10 and N5-LM2 shows that a limestone stoichiometry of 1.9 was required to offset the effect of 50,000 ppm Cl^- at 2500 ppm inlet SO_2 concentration. Tests NB-11 and N5-LM4 were intended to evaluate the effectiveness of high limestone stoichiometry under low sulfur coal conditions (inlet SO_2 concentration at 500 ppm). Table 6-2 indicates that, at 50,000 ppm Cl^-, a limestone stoichiometry of 2.1 was required to raise the SO_2 removal efficiency to the base case level.

6.2 HIGH L/G TESTS

The effectiveness of a high L/G ratio was tested because it can both raise SO_2 removal efficiency and alleviate gypsum scaling in the scrubber bottom through reduced SO_2 make-per-pass.

A set of short term L/G effect tests were performed at 40,000 ppm Cl^-. L/G ratios were changed from 5.3 to 13.3 liter/meter^3 by adjusting the slurry recirculation rate. The limestone feed rate was also adjusted according to the changes of SO_2 removal efficiency to keep a 1.4 stoichiometric ratio. The short term feature of the test made the limestone stoichiometric ratio effect invalid since the scrubber steady state was not achieved during the test. The results shown in Figure 6-2 and Table 6-3 indicate that SO_2 removal efficiency was very sensitive to L/G ratio. A very high L/G (above 15 liter/meter^3) was needed to reach the baseline SO_2 removal (80 percent) at L/G of 8.0.

6.3 LIME ADDITION TESTS

Lime addition to a second hold tank was also suggested as an option to solve the high chloride problem. The SO_2 removal should benefit from the increase of hold tank pH and increased dissolved alkalinity through the addition of lime to the limestone scrubber.

Table 6-2. Operating Conditions of High Limestone Stoichiometry Calcium Chloride Tests with Low SO_2 Make-per-pass

Test	NB-10	N5-LM2	NB-11	N5-LM4
Cl^- concentration, ppm	Basecase	50000	Basecase	50000
L/G ratio, liter/meter^3	10.7	10.7	4.6	4.7
Slurry solids, %	9.6	10.2	9.7	10.1
Scrubber feed pH	5.8	5.2	5.9	5.8
Scrubber effluent pH	5.4	4.7	5.5	5.6
Inlet SO_2, ppm	2500	2500	490	500
SO_2 absorption, %	56.3	56.9	52.3	55.3
SO_2 make-per-pass, mmole/liter	4.54	4.7	1.93	2.0
Limestone stoichiometry	1.20	1.9	1.22	2.1
Height of packing, cm	0	0	0	0
Flue gas O_2, %	10.7	11.0	10.6	10.8
Test period, hours	47	18	33	21
Slurry settling rate, cm/min	0.6	-	0.6	-

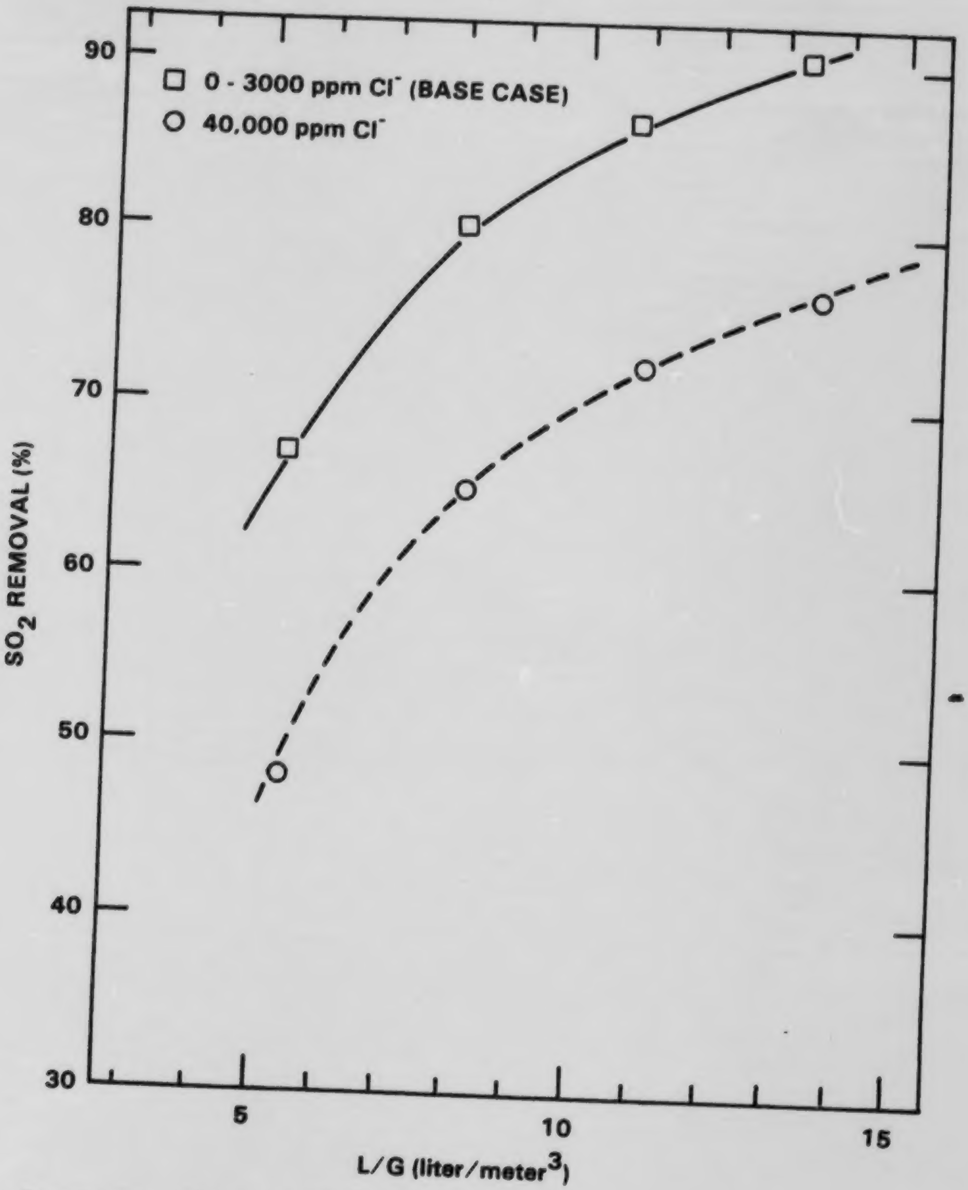


Figure 6-2. Effect of L/G ratio on SO_2 removal with natural oxidation.

Table 6-3. Average Scrubber Performance for L/G Test

L/G, liter/meter^3	4.7	8.0	9.4	13.3
Hours tested	9	71	11	9
SO_2 removal, %	48	66	72	76
Inlet SO_2, ppm	2670	2610	2630	2680
Outlet SO_2, ppm	1390	890	770	650

A series of short term lime addition tests were run at 50,000 ppm Cl^-. Two hold tanks in series were used with residence times of 5 and 3 minutes, respectively. As shown in Figure 6-3, 40% limestone slurry was added to the first hold tank and 30% hydrated lime slurry was added to the second. The lime and limestone feed rates were controlled separately at constant stoichiometric ratios. The overall reagent stoichiometry is the sum of those two ratios. Considerable pH fluctuation was experienced during the test as shown in Table 6-4 which also affected the accuracy of the data. The short term results shown in Figure 6-4 indicated that a lime stoichiometric ratio of 0.7 was required to reach the baseline SO_2 removal (80%). The data point at 0.6 lime stoichiometric ratio (run N5-L5) indicated that the limestone feed rate might be reduced by the addition of lime.

6.5 ORGANIC DIBASIC ACID TEST

The use of mass transfer additives to increase dissolved alkalinity was also considered. Organic dibasic acid was considered a more attractive additive than magnesium since previous data indicate it is very effective in enhancing the SO_2 removal efficiency of limestone scrubbers.(24,25) Organic acids are present in the limestone slurry as anions which react with the acidity generated by SO_2 absorption and enhance the SO_2 removal efficiency in a method similar to increasing dissolved alkalinities. Calculations indicate that the maximum organic acid concentration required to offset depleted alkalinity due to $CaCl_2$ accumulation should be less than 10 meq/l.

Monsanto DBA, which has been tested and commercialized in a full-scale FGD unit(26), was utilized for current testing. Silicic acid titration was used to analyze the concentration of total organic acid in the slurry. The effectiveness of DBA addition on SO_2 removal efficiency enhancement was evaluated by a series of short term tests. The operating conditions and test results are

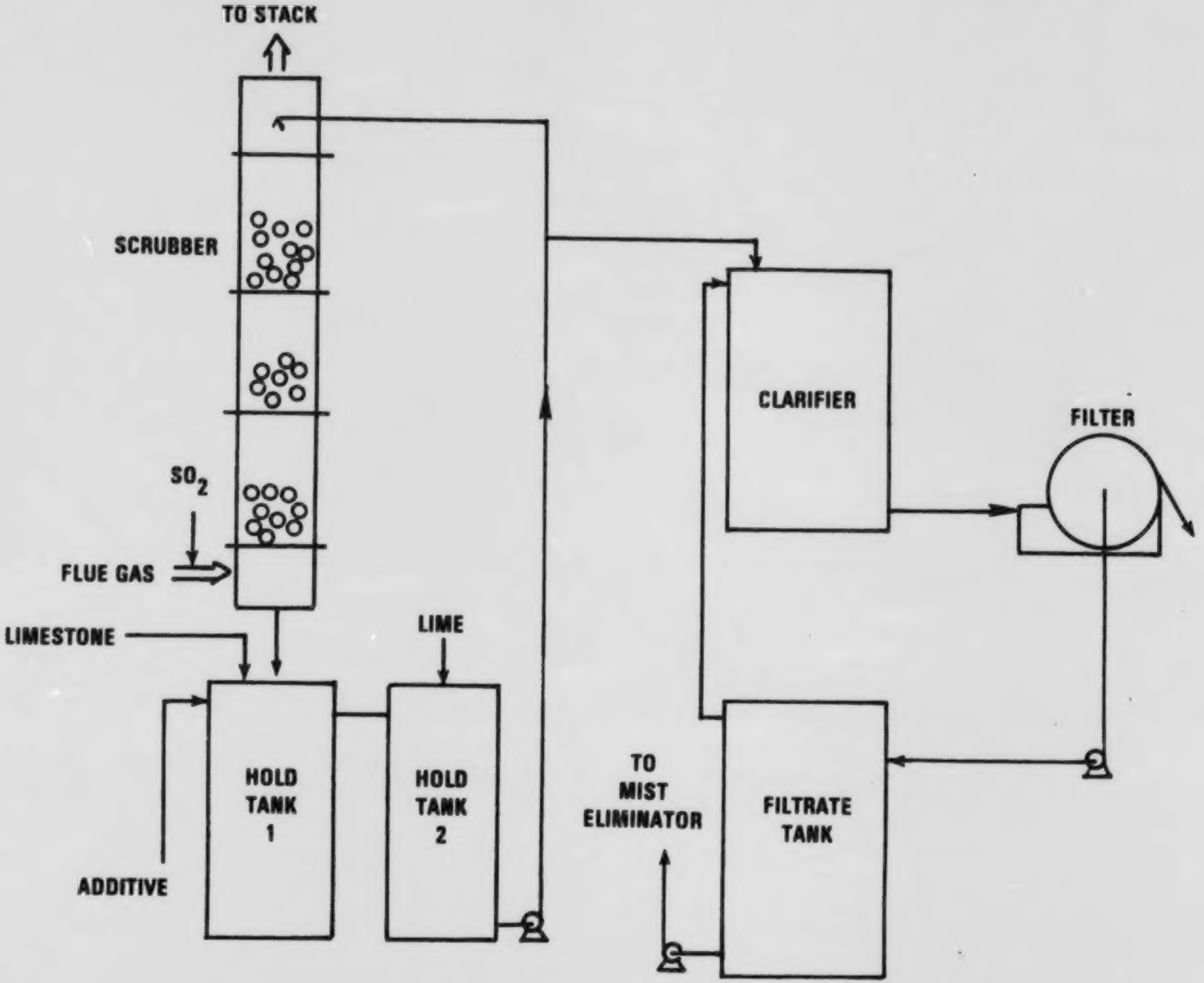


Figure 6-3. Flow diagram for two-hold-tank lime addition test.

Table 6-4. Operating Conditions of Lime Addition Tests

Test	N5-1L	N5-2L	N5-3L	N5-4L	N5-5L
Cl^- concentration, ppm	50000	50000	50000	50000	50000
L/G, liter/meter^3	8.0	8.0	8.0	8.0	8.0
Slurry solids, %	10.6	10.2	10.0	10.5	10.0
Scrubber feed pH	6.4	7.1	7.9	8.0	6.9
Hold tank 1 pH	4.9	5.1	5.9	6.0	5.6
Scrubber effluent pH	4.7	4.9	5.8	5.9	5.0
Inlet SO_2, ppm	2610	2610	2610	2610	2610
SO_2 absorption, %	71	76	8	86	80
SO_2 make-per-pass, mmole/liter	7.8	8.2	39.2	9.4	8.8
Flue gas O_2, %	10.5	11.0	10.0	10.5	10.7
Limestone stoichiometry	1.01	1.01	1.01	1.01	0.79
Lime stoichiometry	0.30	0.52	1.02	1.19	0.63
Slurry settling rate, cm/min	0.17	0.17	0.15	0.2	0.17
Test period, hours	23	23	13	9	10

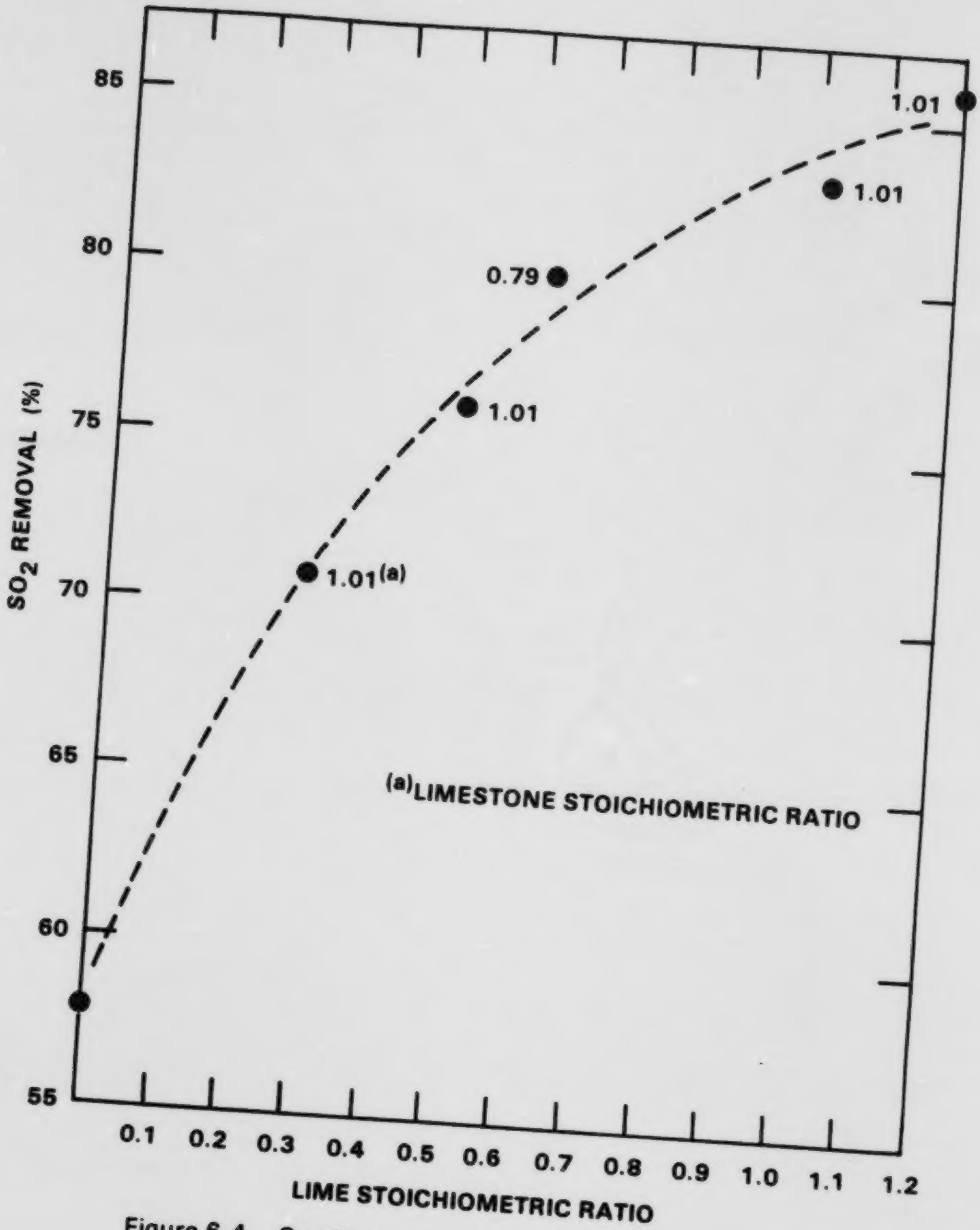


Figure 6-4. Scrubber performance with lime addition.

shown in Table 6-5 and Figure 6-5. Figure 6-5 indicates that DBA is a very effective additive for mass transfer enhancement even at 50,000 ppm Cl^-. Less than 6 meq/l of total organic acid was required to raise the SO_2 removal efficiency from 58% to 70%. The SO_2 removal efficiency reached 88% at 12.7 meq/l of organic acid.

The second series of tests was run to evaluate the amount of DBA required to offset the calcium chloride effect on SO_2 removal efficiency at various Cl^- concentrations. The limestone scrubber was first operated without chloride addition to establish baseline conditions. Then, calcium chloride was added to raise the chloride ion concentration to predetermined levels and the characteristic drop of SO_2 removal efficiency was observed. DBA was then added to the hold tank to restore the SO_2 removal efficiency to the baseline level. The effectiveness of DBA was evaluated at four different chloride concentrations under natural oxidation and five under forced oxidation. Operating conditions are shown in Tables 6-6 and 6-7.

The result, as shown in Figure 6-6, indicated that DBA is very effective in counteracting the chloride effect under both natural and forced oxidation conditions. In order to maintain baseline SO_2 removal efficiency, more DBA was required at higher chloride ion concentrations. Figure 6-6 showed that only 9.2 meq/l DBA (equivalent to 672 ppm adipic acid) was needed to compensate for the effect of 80,000 ppm Cl^- under natural oxidation, and only 9.4 meq/l DBA (equivalent to 686 ppm adipic acid) was needed to compensate for 160,000 ppm Cl^- under forced oxidation. At equivalent Cl^- concentrations, less DBA was needed with forced oxidation than with natural oxidation. This is reasonable since less Cl^- effect on SO_2 removal efficiency was observed with forced oxidation. No significant changes in filter cake quality were observed during the DBA addition.

Table 6-5. Operating Conditions of Natural Oxidation DBA Effectiveness Tests

Test	N5-1	N5-1A	N5-2A	N5-3A
Cl^- concentration, ppm	50000	50000	50000	50000
L/G liter/meter^3	8.0	8.0	8.0	8.0
Slurry solids, %	10.4	10.1	9.6	10.1
Scrubber feed pH	4.9	4.9	4.9	5.1
Scrubber effluent pH	4.5	4.4	4.4	4.6
Inlet SO_2, ppm	2570	2500	2450	2530
SO_2 absorption, %	58.0	70.1	80.5	88.2
SO_2 make-per-pass, mmole/liter	6.2	7.4	8.4	9.3
Limestone stoichiometry	1.39	1.40	1.40	1.40
Solids settling rate, cm/min	0.6	0.2	0.2	0.2
Flue gas O_2, %	9.5	9.9	9.9	9.6
HCl feed rate, lb/hr	0.40	0.41	0.41	0.42
Filter cake solids, %	52.3	52.9	56.0	52.0
DBA concentration, meq/liter	0	5.8	8.8	12.7
Corresponding adipic acid Concentration, ppm	0	424	643	928

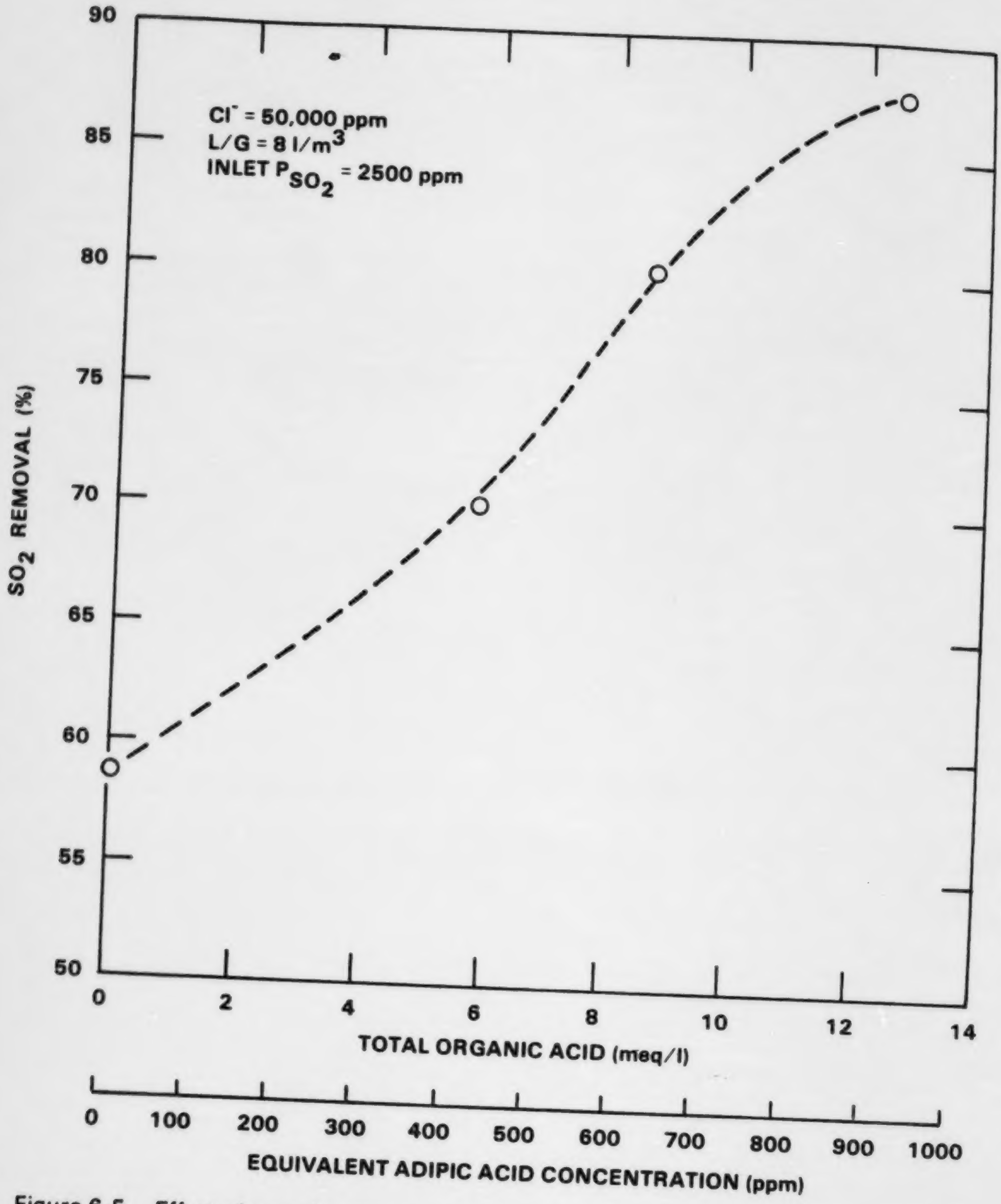


Figure 6-5. Effect of organic acid concentration on sulfur dioxide removal at 50,000 ppm chloride by Monsanto DBA addition.

Table 6-6. Operating Conditions of Natural Oxidation DBA Effectiveness Tests

Test	NB-1A	N2-1A	N5-4A	N8-1A
Cl^- concentration, ppm	Basecase	20000	50000	80000
L/G, liter/meter^3	8.0	8.0	8.0	8.0
Slurry solids, %	9.9	10.2	10.3	9.8
Scrubber feed pH	6.0	5.4	5.0	4.8
Scrubber effluent pH	5.6	4.9	4.5	4.3
Inlet SO_2, ppm	2580	2560	2510	2540
SO_2 absorption, %	80.2	81.2	81.0	81.0
SO_2 make-per-pass, mmole/liter	8.5	8.7	8.6	8.6
Limestone stoichiometry	1.31	1.30	1.30	1.30
Flue gas O_2, %	5.6	5.8	5.5	5.7
Oxidation, %	11.3	-	12.0	-
Filter cake solids, %	54.5	55.6	56.2	54.3
DBA concentration meq/l	0	3.3	7.2	9.2
Corresponding adipic acid concentration, ppm	0	241	526	672

Table 6-7. Operating Conditions of Forced Oxidation DBA Effectiveness Tests

Test	FB-1A	F5-1A	F8-1A	F10-1A	F16-1A
Cl^- concentration, ppm	Basecase	50000	80000	100000	160000
L/G, liter/meter^3	8.0	8.0	8.0	8.0	8.0
Slurry solids, %	9.6	10.1	10.3	10.1	10.2
Scrubber feed pH	6.0	5.7	5.6	5.5	5.4
Scrubber effluent pH	5.2	4.7	4.5	4.4	4.2
Inlet SO_2, ppm	2530	2560	2510	2560	2540
SO_2 absorption, %	80.5	81.2	81.5	81.2	80.5
SO_2 make-per-pass, mmole/liter	8.5	8.6	8.7	8.7	8.5
Limestone stoichiometry	1.19	1.18	1.18	1.18	1.19
Flue gas O_2, %	5.4	5.5	6.4	7.1	6.6
Oxidation, %	98	-	96.7	-	96.2
Filter cake solids, %	77.3	81.2	77.4	81.2	79.3
DBA concentration meq/l	0	3.2	5.6	6.1	9.4
Corresponding adipic acid concentration, ppm	0	234	409	445	686

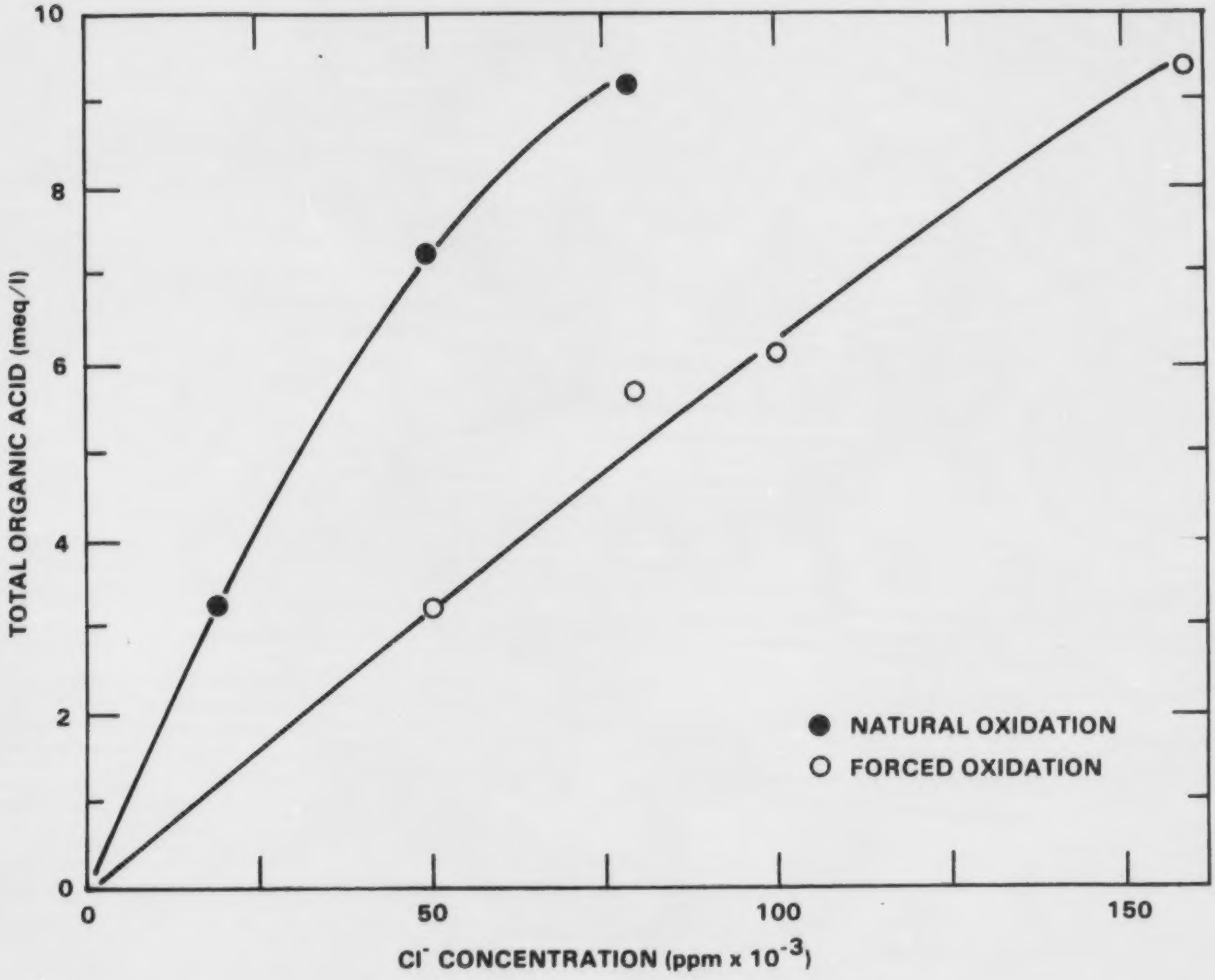


Figure 6-6. Organic acid concentrations required to maintain 80% SO_2 removal efficiency at high chloride ion concentrations.

SECTION 7

CALCIUM CHLORIDE EFFECTS ON LIME SCRUBBER PERFORMANCE

Lime is a much more reactive reagent than limestone for FGD systems. Better reagent utilization is therefore usually obtained. Pilot plant tests were conducted to evaluate the effects of calcium chloride on the performance of a lime scrubber under natural oxidation conditions for both high and low sulfur coal cases. The low sulfur coal condition was simulated by controlling the flue gas SO_2 concentration at about 500 ppm. High sulfur coal conditions were simulated by controlling the flue gas SO_2 concentration at about 2500 ppm. Control of hold tank pH was utilized since the extreme sensitivity of hold tank pH and SO_2 removal efficiency to stoichiometry at the chosen test point (stoichiometry of approximately 1.0) precluded stoichiometry control. Stoichiometry control would have prevented the system from reaching steady state conditions, whereas control of hold tank pH was more stable and resulted in steady state operation.

7.1 HIGH SULFUR COAL TESTS

Five runs were made evaluating the chloride ion effects at the 2500 ppm inlet flue gas SO_2 concentration. Operating conditions are listed in Tables 7-1 and 7-2. Significant effects of calcium chloride accumulation on SO_2 removal efficiency and scrubber effluent pH were observed.

Figure 7-1 indicates that the SO_2 removal efficiency dropped with the accumulation of Cl^-. At 20,000 ppm Cl^-, 77% SO_2 removal efficiency was obtained which was 3 percentage points lower than the base case removal efficiency (80%). At 40,000 ppm Cl^- the SO_2 removal efficiency decreased to 66%. A further drop of SO_2 removal efficiency was observed with the increase of Cl^- concentration. At 80,000 ppm Cl^-, only 55% SO_2 removal efficiency was

Table 7-1. Operating Conditions of High Chloride Lime Tests Under High Sulfur Coal Conditions

Test ID	LB-1	L2-1	L4-1	L6-1	L8-1
Chloride level, ppm	Baseline	20000	40000	60000	80000
L/G, liter/meter^3	8.0	8.0	8.0	8.0	8.0
Slurry solids, %	10.1	9.8	9.9	10.2	9.8
Scrubber feed, pH	5.7	5.7	5.8	5.6	5.6
Scrubber effluent pH	4.7	3.8	3.7	3.3	3.2
Inlet SO_2, ppm	2550	2500	2470	2500	2440
SO_2 absorption, %	80	77	66	64	55
SO_2 make-per-pass, mmole/liter	8.2	7.8	7.0	6.6	5.6
Lime stoichiometry	0.97	1.01	1.06	1.01	1.0
Height of packing, cm	53.3	53.3	53.3	53.3	53.3
Flue gas O_2, %	5.1	4.7	5.1	-	5.5
Oxidation, %	14.4	17.3	-	17.2	14.1
Filter cake solids, %	59.4	58.6	60.2	60.3	61.0

Table 7-2. Summary of Liquor Analyses for High Chloride Lime Tests under High Sulfur Coal Conditions

Run	LB-1		L2-1		L6-1		L8-1	
Component, ppm	HT	SE	HT	SE	HT	SE	HT	SE
Ca	716	905	11200	11300	31900	32500	44600	44600
Mg	915	908	792	825	958	965	1060	1080
Na	82	86	425	405	937	947	1630	1630
SO_3	414	1300	25	806	51	783	0	565
SO_4	2830	3320	840	1130	439	768	665	723
CO_3	53	63	39	55	32	32	40	45
Cl	1700	1790	20200	20000	60400	60300	80700	80500
pH	5.7	4.7	5.7	3.8	5.8	3.3	5.6	3.2
$CaSO_4 \cdot 2H_2O$ Saturation, %	71.1	97.7	83.9	111.8	64.7	114.5	106.6	115.3

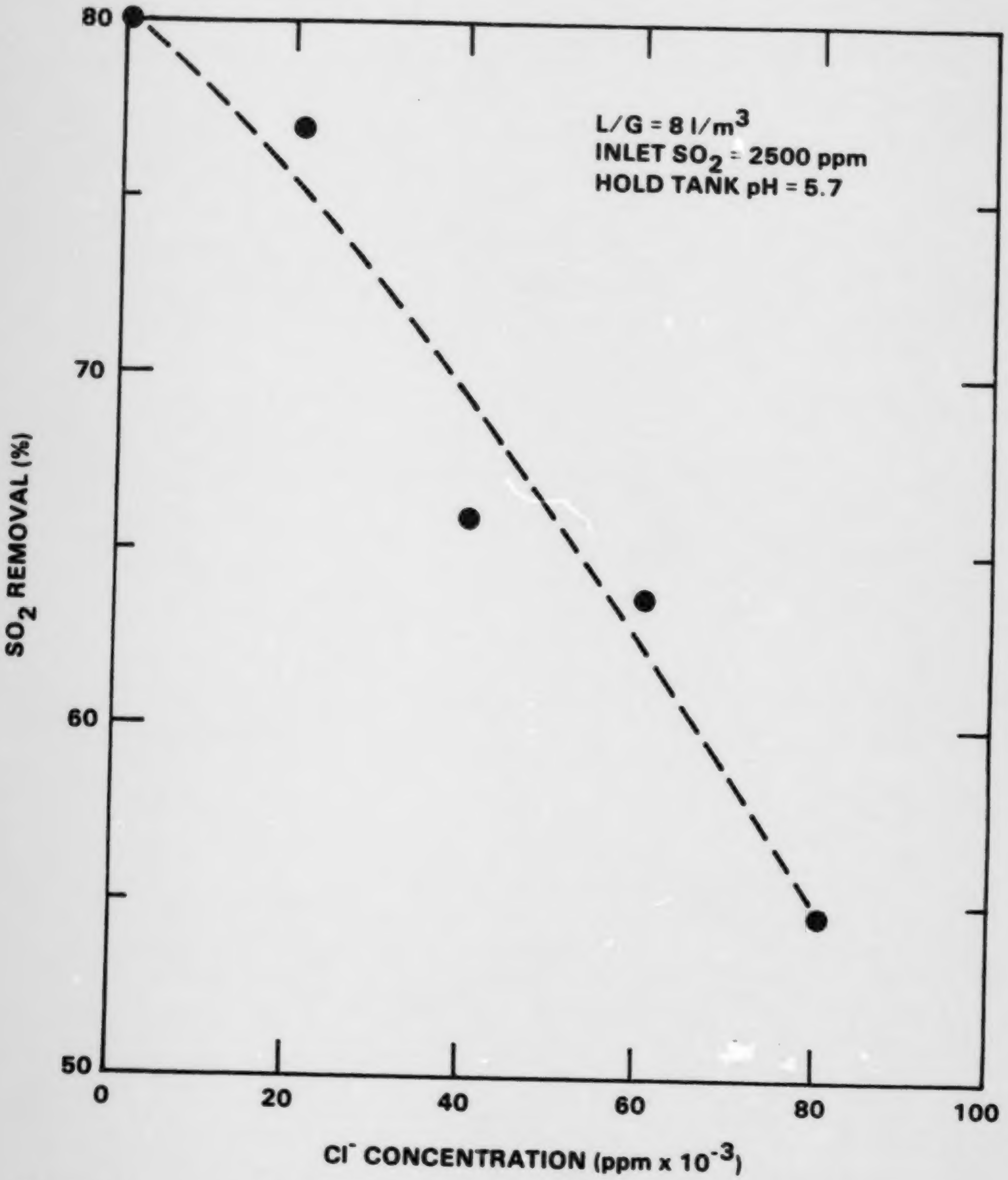


Figure 7-1. Effect of chloride ion on the SO_2 removal efficiency of RTP lime scrubber.

obtained. Figure 7-2 shows the effect of Cl^- on system pH. With hold tank pH set at 5.7, the scrubber effluent pH decreased continuously from 4.7 (base case) to 3.2, while the Cl^- concentration increased from 1700 to 80,000 ppm. The lime stoichiometries utilized for high sulfur coal tests are shown in Figure 7-3.

7.2 LOW SULFUR COAL TESTS

Four runs were made to evaluate the calcium chloride effects at the 500 ppm inlet flue gas SO_2 concentration. Operating conditions are shown in Table 7-3.

Only the decrease of scrubber effluent pH was observed with the increase of Cl^- concentration for low sulfur coal tests. At 500 ppm inlet gas SO_2 concentration and L/G of 4.3 liter/meter^3, the SO_2 removal efficiency reached 81.3% at 100,000 ppm Cl^- which is not significantly different from the 80.6% at 250 ppm Cl^- (base case). But the scrubber effluent pH was 3.7 at 100,000 ppm Cl^- which was considerably lower than the 5.1 observed at 250 ppm Cl^-.

No significant effect of Cl^- on solids quality was observed for either high or low sulfur coal tests.

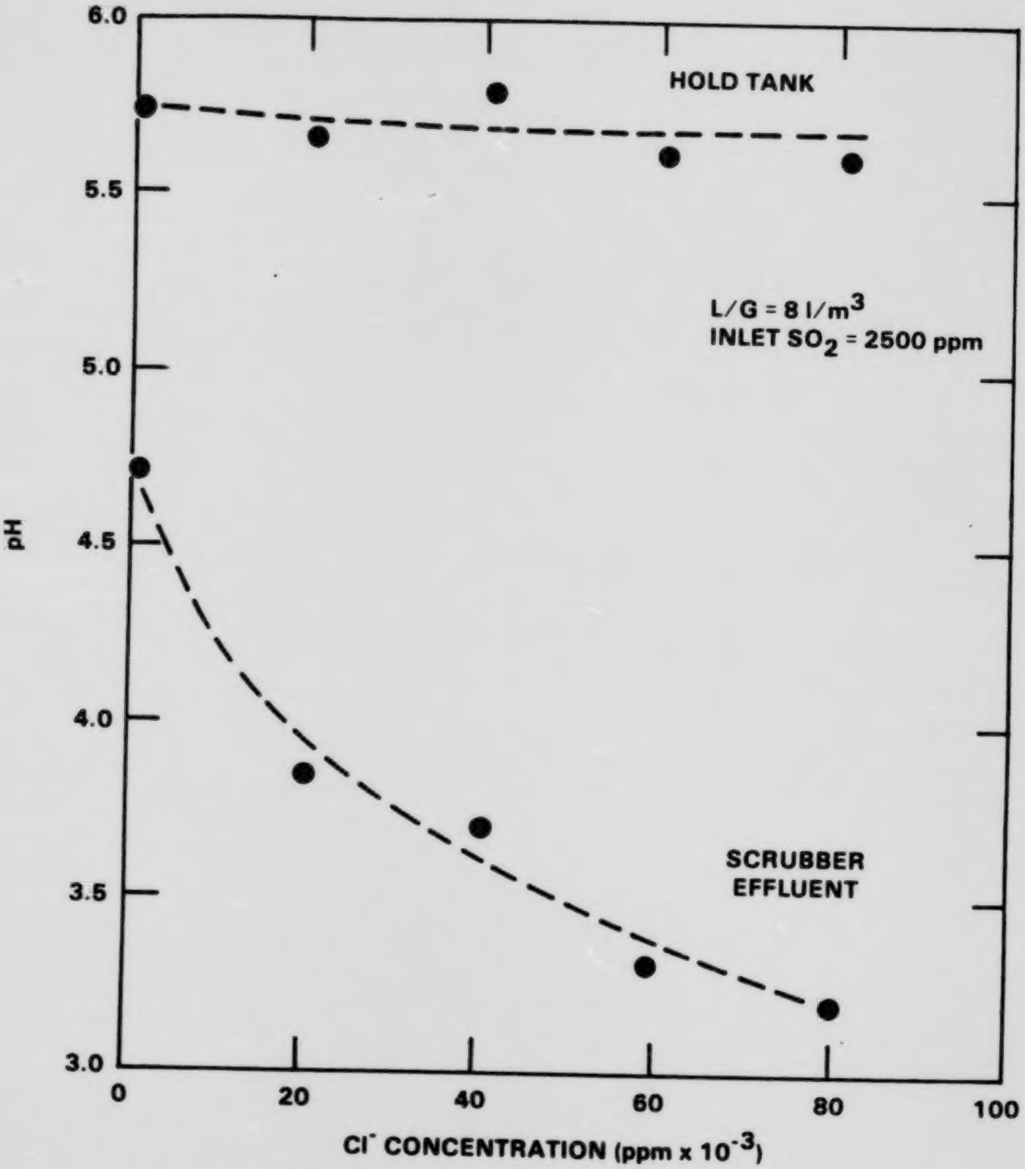


Figure 7-2. Chloride ion effect on system pH of RTP lime scrubber.

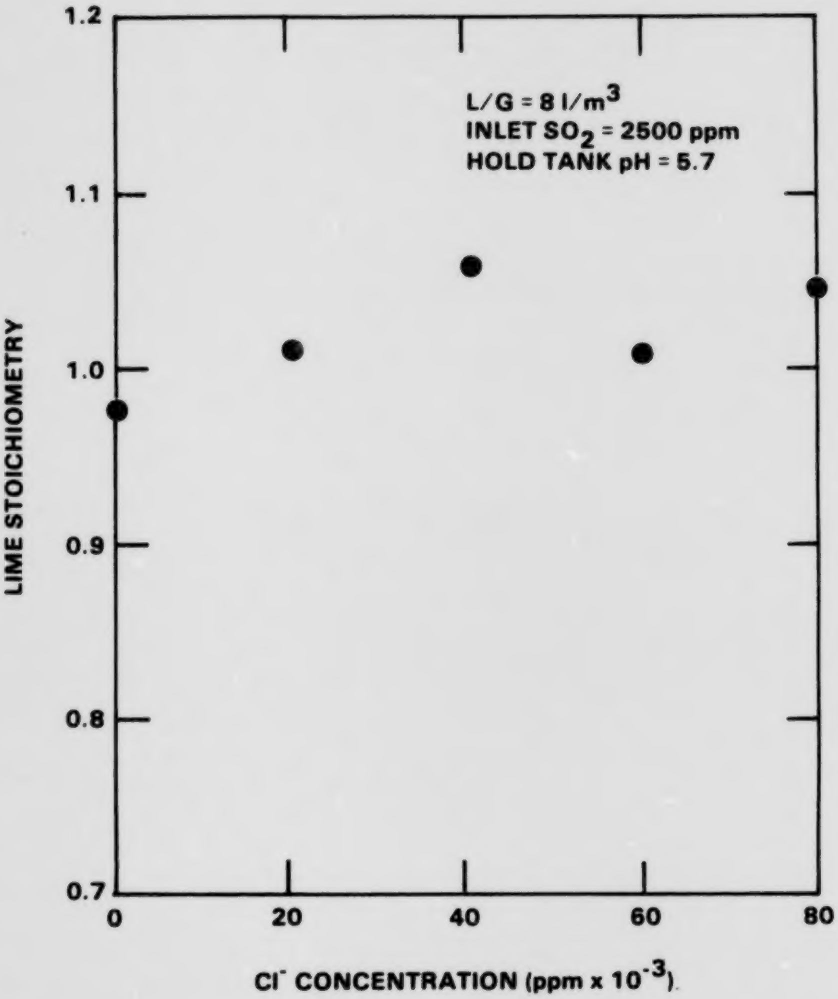


Figure 7-3. Lime stoichiometry for high sulfur coal tests.

Table 7-3. Operating Conditions of High Chloride Lime Tests Under Low Sulfur Coal Conditions

Test ID	LB-2	L3-1	L7-1	L10-1
Chloride level, ppm	Baseline	30000	70000	100000
L/G, liter/meter^3	4.4	4.4	4.4	4.4
Slurry solids, %	9.8	9.5	9.3	9.7
Scrubber feed, pH	5.7	5.75	5.7	5.7
Scrubber effluent pH	5.1	4.0	3.7	3.7
Inlet SO_2, ppm	540	530	500	520
SO_2 absorption, %	81	81	82	81
SO_2 make-per-pass, mmole/liter	3.1	3.1	3.1	3.1
Lime stoichiometry	1.03	1.00	1.01	1.02
Height of packing, cm	53.3	53.3	53.3	53.3
Flue gas O_2, %	5.7	5.1	4.9	5.2
Oxidation, %	8.9	-	14.7	-
Filter cake solids, %	62.7	63.7	62.4	62.4

SECTION 8

EFFECTS OF CALCIUM CHLORIDE ON MAGNESIA ENHANCED LIMESTONE SCRUBBER PERFORMANCE

The addition of magnesia to a lime/limestone scrubber increases the concentrations of two dissolved sulfite species, SO_3^{2-} and $MgSO_3$, which react with the absorbed SO_2 and facilitate the absorption of SO_2. The accumulation of chloride, especially calcium chloride, affects the magnesia enhanced limestone scrubbing process by reducing concentrations of both SO_3^{2-} and $MgSO_3$. The system chemistry is governed by ion balance, solubility product and equilibrium relationships which can be expressed as:

$$A_{Ca}^{2+} \cdot A_{SO_3}^{2-} = K_{sp}' \qquad (8\text{-}1)$$

$$A_{Ca}^{2+} \cdot A_{SO_4}^{2-} = K_{sp}'' \qquad (8\text{-}2)$$

$$A_{Mg}^{2+} \cdot A_{SO_3}^{2-} = K'^{\circ} M_{g}SO_3^{\circ} \qquad (8\text{-}3)$$

$$A_{Mg}^{2+} \cdot A_{SO_4}^{2-} = K''^{\circ} M_{g}SO_3^{\circ} \qquad (8\text{-}4)$$

When HCl is absorbed from flue gas, the dissolution of additional limestone is required to neutralize the hydrochloric acid formed in the scrubber. However, due to the extremely low solubility products of calcium sulfite and sulfate, the sulfite and sulfate ion concentrations will be reduced by precipitation with the calcium derived from dissolution of extra limestone. The ion balance will be maintained since the negative ions precipitated are replaced by chloride ions. Equilibrium constraints require that the magnesium sulfite and sulfate shown in Equations (8-3) and (8-4) shift toward the left and cause a reduction of the magnesium sulfite ion pair. Therefore, the net result is the displacement of the sulfite ion magnesium sulfite ion pair from the limestone slurry and the accumulation of magnesium chloride. After most sulfite and magnesium sulfite have been depleted, the accumulation of Cl^- should result in a stoichiometric increase of Ca^{2+} concentration.

8.1 EFFECT OF CHLORIDE ION ON THE DEPLETION OF SULFITE AND MAGNESIUM SULFITE

Four runs were made evaluating the effects of chloride on a magnesia enhanced limestone scrubber. Operating conditions are listed in Table 8-1. In the base case (run MG-1) the magnesium concentration was maintained at 2000 ppm and SO_2 removal efficiency reached 93.3%. Eighty-four percent SO_2 removal efficiency is expected without magnesia enhancement. The Cl^- concentration was increased to 9000 ppm for run MG-2. As shown in Table 8-2, scrubbing liquor analysis indicated that the sulfite and sulfate concentrations dropped sharply. The sharp drop of sulfite concentrations was reflected by the significant decrease of SO_2 removal efficiency as shown in Figure 8-1. Figure 8-2 shows that the hold tank pH dropped from 5.75 to 5.6.

8.2 EFFECT OF CALCIUM CHLORIDE ACCUMULATION

Further increase of Cl^- concentration resulted in an almost stoichiometric accumulation of calcium ion but little change of sulfite and sulfate ion concentrations as shown in Table 8-2 (runs MG-3 and -4). Additional decreases of SO_2 removal efficiency and hold tank pH were obtained with increasing Cl^- concentrations. Figures 8-1 and 8-2 indicate that, at 50,000 ppm Cl^-, only 67.7% SO_2 removal efficiency and 5.1 hold tank pH were observed.

The hold tank pH values were plotted against the sum of Ca^{2+} and Mg^{2+} concentrations in Figure 8-3. It is shown in Figure 8-3 that the pH values observed during the magnesia enhanced limestone tests agree very well with the correlation obtained from calcium, magnesium and sodium chloride tests.

Table 8-1. Major Operating Conditions of Magnesia Enhanced Limestone Tests

Test ID	MG-1	MG-2	MG-3	MG-4
Chloride level, ppm	Baseline	9000	22000	50000
Magnesium level, ppm	2000	2000	2000	2000
L/G, liter/meter^3	10.3	9.9	10.0	10.0
Slurry solids, %	9.8	9.8	9.8	9.6
Scrubber feed, pH	5.75	5.6	5.4	5.1
Scrubber effluent pH	5.5	5.2	4.9	4.9
Inlet SO_2, ppm	2530	2510	2510	2490
SO_2 absorption, %	93.3	78.3	76.3	67.7
SO_2 make-per-pass,	8.73	8.03	7.8	6.6
Limestone stoichiometry	1.18	1.22	1.23	1.22
Height of packing, cm	53.3	53.3	53.3	53.3
Flue gas O_2, %	10.7	9.0	9.6	7.1
Oxidation, %	20.6	18.5	11.7	13.6
Filter cake solids, %	55.7	56.1	57.1	56.3

Table 8-2. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Composition of Magnesia Enhanced Limestone Tests

Test	MG-1		MG-2		MG-3		MG-4	
Component, ppm	HT	SE	HT	SE	HT	SE	HT	SE
Ca	580	754	2730	2794	9560	9800	2340	2330
Mg	1970	2050	2030	2100	1980	2030	1970	1970
Na	29	30	165	160	395	405	677	690
Cl	1270	1270	9070	9080	22700	22400	49500	49700
SO_3	664	1140	230	608	91	375	94	299
SO_4	7310	8500	1860	2730	1730	2650	-	-
CO_3	232	157	212	126	267	151	167	122

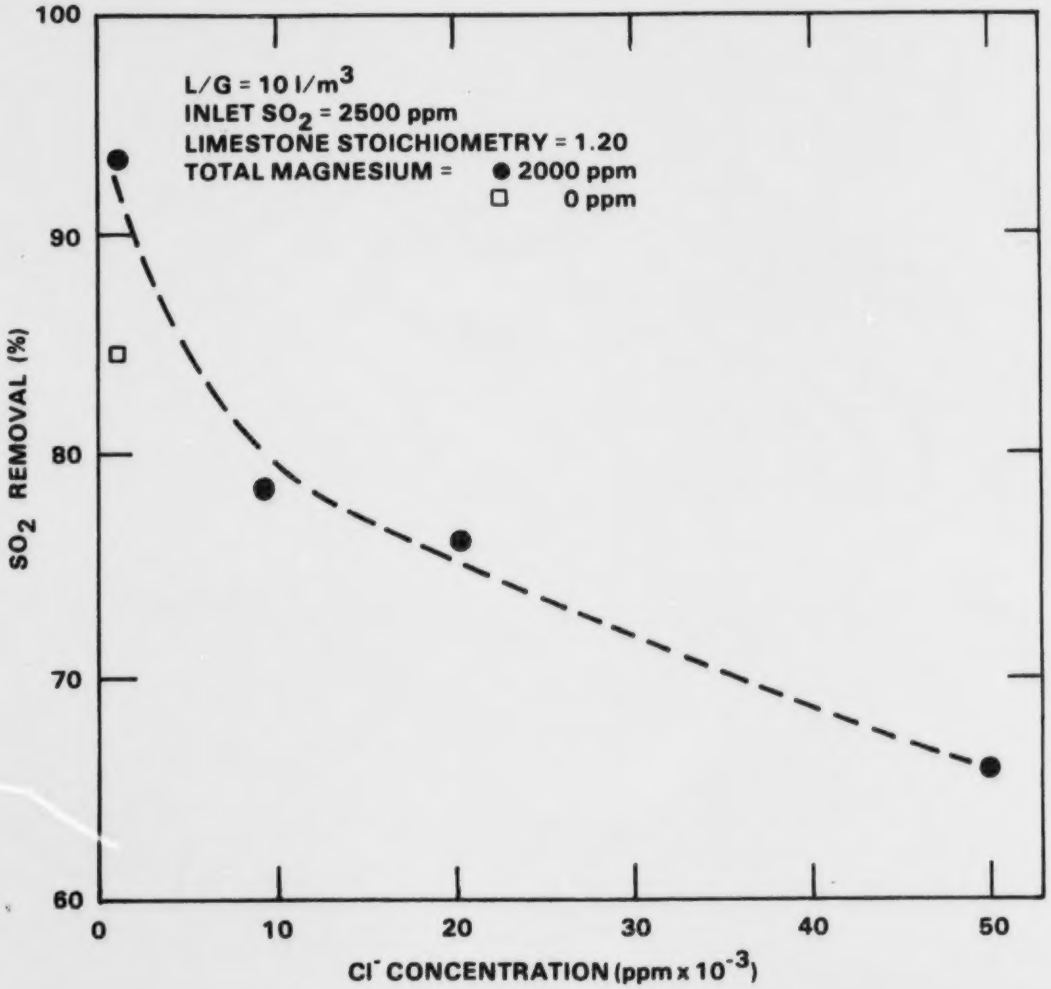


Figure 8-1. Effect of chloride ion on the SO_2 removal efficiency of a magnesia enhanced limestone scrubber.

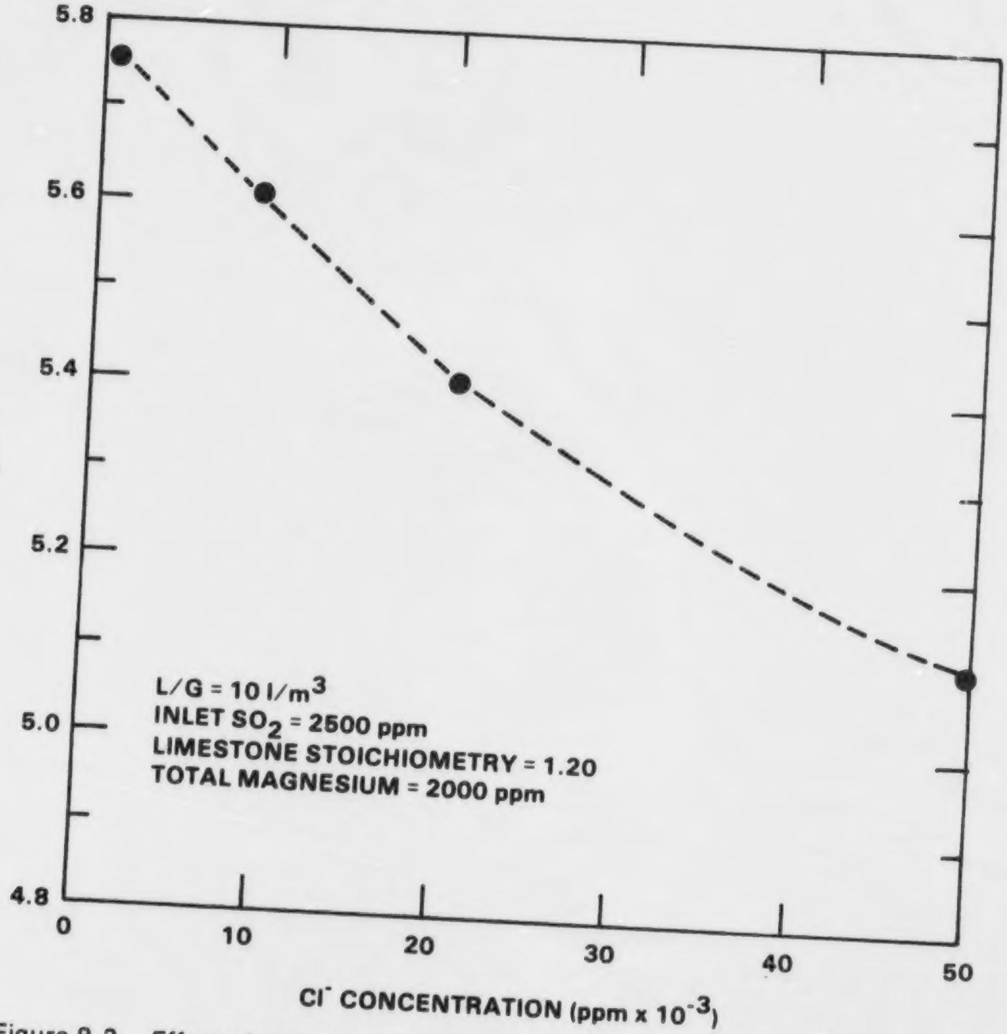


Figure 8-2. Effect of chloride ion on the hold tank pH of a magnesia enhanced limestone scrubber.

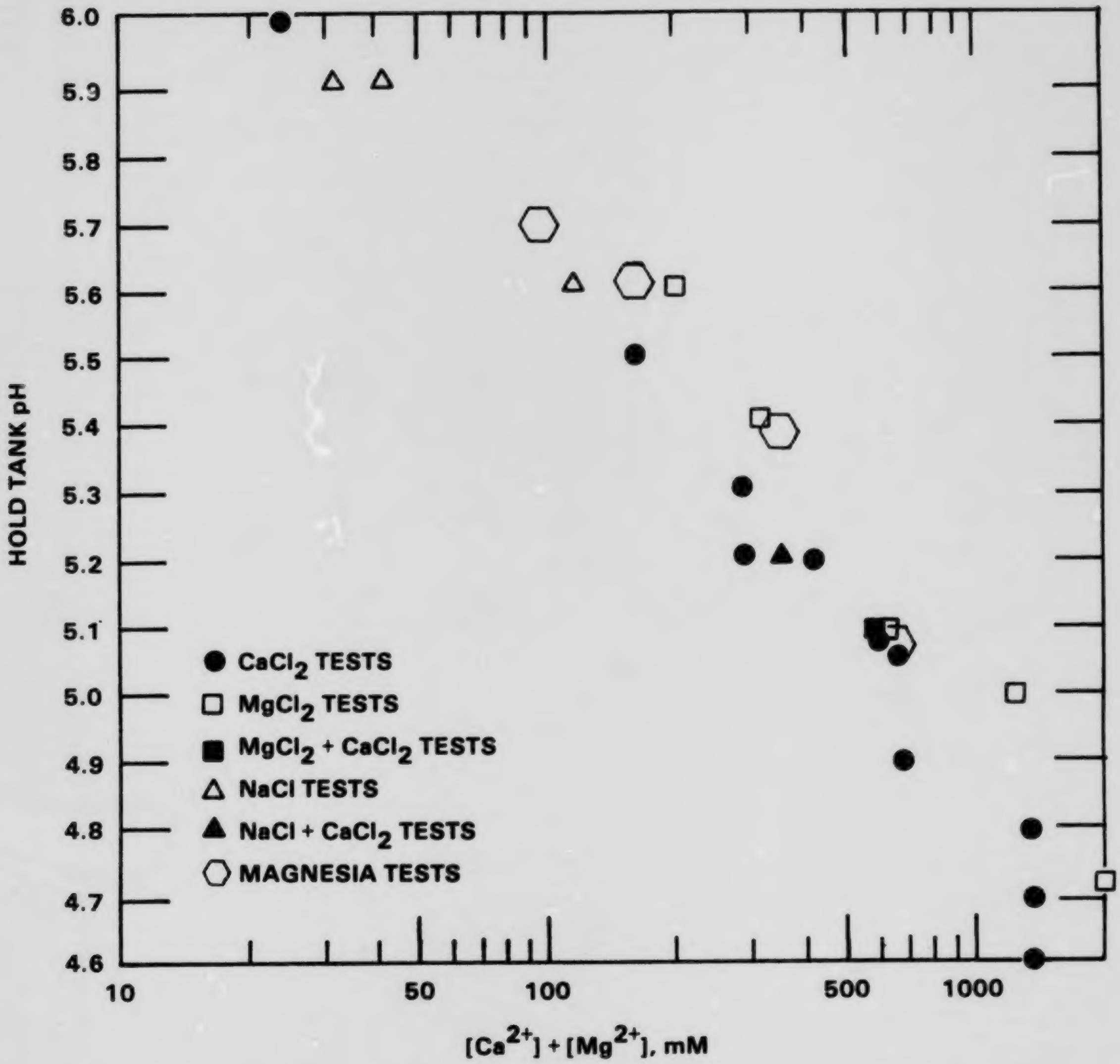


Figure 8-3. Comparison of natural oxidation hold tank pH's as a function of calcium and magnesium ion concentrations.

Figure 8-3 confirms that pH values of the limestone scrubber was determined by the sum of Ca^{2+} and Mg^{2+} concentrations and $CO_3^{2-}/HCO_3^-/CO_2$ equilibrium under natural oxidation conditions.

SECTION 9

CALCIUM CHLORIDE EFFECTS ON DBA ENHANCED LIMESTONE SCRUBBER PERFORMANCE

Organic dibasic acid (DBA) has been demonstrated to be a very effective mass transfer additive for limestone FGD systems. Data has indicated that the major benefits of DBA enhanced limestone scrubbing having included increased SO_2 removal efficiency, decreased limestone consumption, decreased waste sludge volume, reduced operating cost, and expanded FGD system flexibility.(24) In order to reduce the organic acid consumption rate in these systems a tight water loop is very desirable. This coincides with the fact that secondary dewatering systems such as vacuum filters or centrifuges with cake washing devices are usually recommended to further reduce sludge volume. The reduced waste sludge volume and tight water loop could, however, result in accumulation of dissolved solids concentration in the limestone slurry, especially when Cl^- is added to the system either from flue gas or makeup water.

As discussed in previous sections, one of the observed Cl^- effects on scrubber performance was the drop of system pH. It is understood that DBA enhances SO_2 removal efficiency by its buffering effect on liquid phase mass transfer. It is the portion of DBA existing in basic form that is the effective mass transfer enhancement additive. Equilibrium relationships indicate that the percent of basic form DBA should decrease with a drop of system pH(25). In order to maintain an effective DBA concentration, the total DBA concentrations must be increased with the drop of pH. Therefore, it is expected that a higher DBA concentration and DBA consumption will be required at higher Cl^- concentrations. It was the objective of this test series to evaluate the effects of calcium chloride on system performance of DBA enhanced limestone scrubbing, especially to quantify the DBA concentration required and DBA consumption rate.

The operating conditions of a DBA enhanced limestone scrubber feature high SO_2 removal efficiency, low limestone stoichiometry and relatively low system pH. In order to simulate the DBA enhanced limestone scrubber, the base case hold tank pH was controlled at 5.2, limestone stoichiometry at less than 1.1 and SO_2 removal efficiency at 90% for both natural and forced oxidation tests. Granulated calcium chloride was added to the hold tank to increase the Cl^- concentration to predetermined levels. Monsanto DBA, which has been tested and commercialized in a full-scale FGD unit(26), as used as the source of DBA. The DBA concentration was adjusted, as necessary, to maintain base case SO_2 removal efficiency.

9.1 CALCIUM CHLORIDE EFFECTS ON SYSTEM PERFORMANCE

Five runs were made to evaluate the effects of calcium chloride concentration on the performance of DBA enhanced limestone scrubbing under natural oxidation conditions. Operating conditions and summaries of liquor analysis are shown in Tables 9-1 and 9-2. Comparisons of data between runs NB-11 and NB-5A indicate that only 10.7 meq/l of DBA (equivalent to 781 ppm adipic acid) was required to enhance the SO_2 removal efficiency from 49.5% to 90.7% at base cases conditions. Calcium chloride was added to the hold tank to raise the Cl^- concentration to 20,000, 50,000 and 80,000 ppm for runs N2-2A, N5-5A and N8-2A, respectively. Figure 9-1 indicates that an increase of DBA concentration was required with the accumulation of calcium chloride to maintain 90% SO_2 removal efficiency. The DBA concentration was raised to 12.1 and 14.8 meq/l as the Cl^- concentration increased to 20,000 and 50,000 ppm, respectively. Another effect observed with the increase of calcium chloride concentration was the drop of hold tank pH. Figure 9-2 shows that the hold tank pH dropped from 5.2 to 4.7 when the Cl^- concentration was increased from base case to 50,000 ppm. Hard scale was found on the bottom screen and

Table 9-1. Operating Conditions for Natural Oxidation DBA Enhanced Limestone Scrubber Tests

Test	NB-11	NB-5A	N2-2A	N5-5A	N8-2A
Cl^- concentration, ppm	Basecase	Basecase	20000	50000	80000
L/G, liter/meter^3	8.3	8.3	8.3	8.3	8.2
Slurry solids, %	9.8	9.5	9.8	9.6	11.7
Scrubber feed pH	5.2	5.2	5.1	4.7	4.4
Scrubber effluent pH	4.6	4.6	4.6	4.2	3.9
Inlet SO_2, ppm	2520	2520	2480	2520	2470
SO_2 absorption, %	49.5	90.7	90.1	89.7	81.8
SO_2 make-per-pass, mmole/liter	5.3	9.9	9.3	9.1	8.6
Limestone stoichiometry	1.10	1.09	1.08	1.08	1.20
Height of packing, cm	53.3	53.3	53.3	53.3	53.3
Flue gas O_2, %	7.3	7.0	7.2	7.1	7.4
Oxidation, %	-	-	15.0	19.0	6.9
Filter cake solids, %	53.6	54.5	54.7	55.4	55.3
DBA concentration, meq/l	0	10.7	12.1	14.8	29.2
Corresponding adipic acid concentration, ppm	0	781	883	1080	2130
Slurry settling rate, cm/min	0.5	0.5	0.5	0.4	0.3

Table 9-2. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Natural Oxidation DBA Enhanced Limestone Tests

Test	NB-5A		N2-2A		N5-5A		N8-2A	
Component, ppm	HT	SE	HT	SE	HT	SE	HT	SE
Ca	1660	1610	10700	10900	26900	26800	41900	41100
Mg	611	581	492	500	655	669	874	840
Na	57	56	428	422	738	709	1540	1450
Cl	1640	1580	26100	20500	50300	50800	80400	80900
SO_3	970	1390	266	725	202	521	165	694
SO_4	1730	1830	1210	1480	841	967	780	794
CO_3	395	205	350	179	307	140	266	178

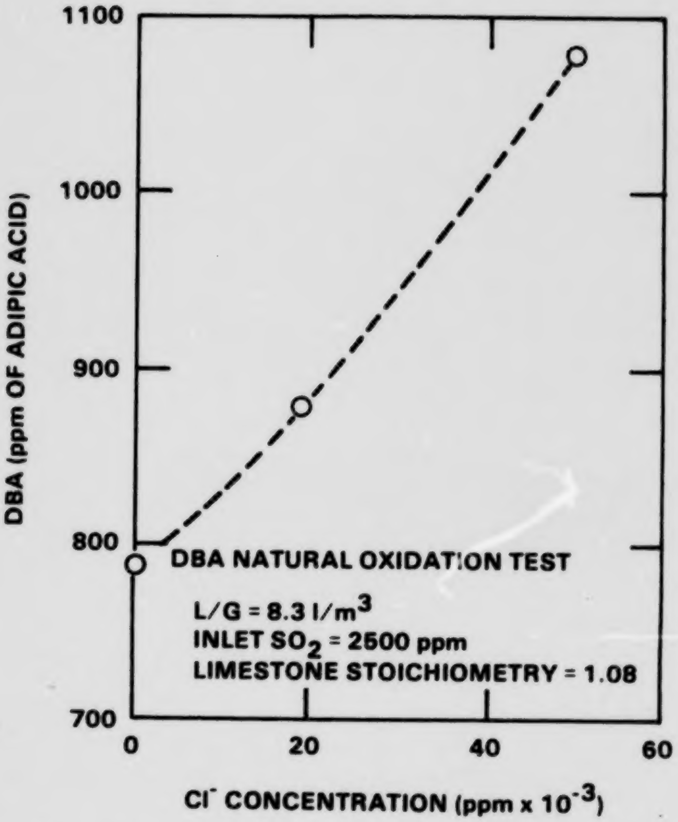


Figure 9-1. DBA required to reach 90% SO_2 removal at high chloride concentrations.

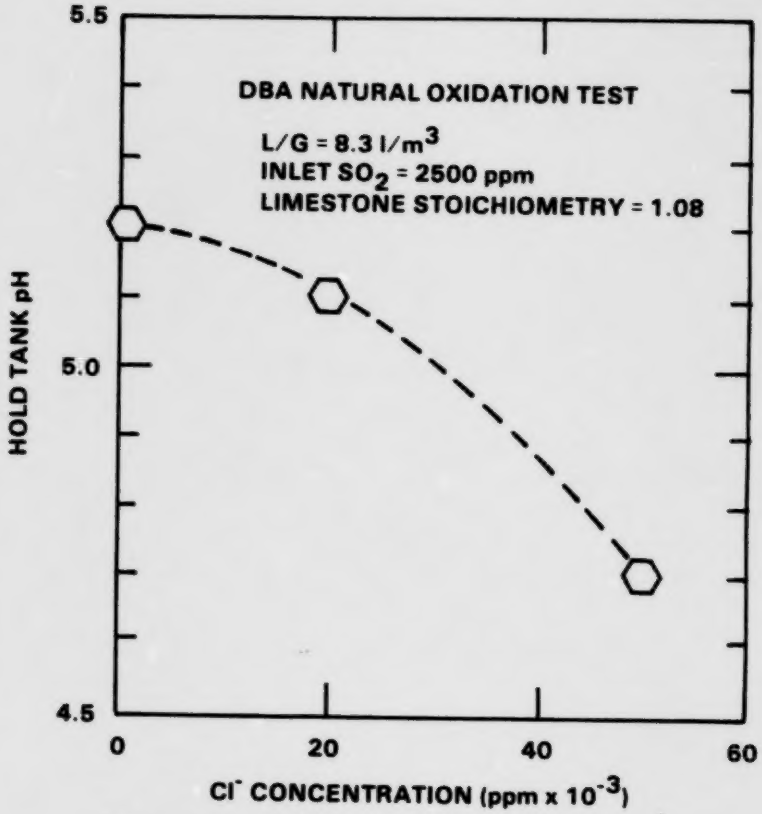


Figure 9-2. Chloride effect on hold tank pH of DBA enhanced limestone scrubber.

downcomer during the pilot plant test with Cl^-concentrations above 50,000 ppm. Analysis of the scale deposits showed significant amounts of sulfate species. Due to the operation problems caused by scaling, the test at 80,000 ppm Cl^- was aborted before 90% SO_2 removal efficiency was achieved.

Similar effects of Cl^- were observed during forced oxidation DBA enhanced limestone scrubbing. Six runs were made to evaluate the effects of calcium chloride. Operating conditions and summaries of liquor analyses are shown in Tables 9-3 and 9-4. Figure 9-3 indicates that an increase of DBA concentration was required with the accumulation of calcium chloride to maintain 90% SO_2 removal efficiency. With forced oxidation, about 10.3 meq/l of DBA (equivalent to 750 ppm adipic acid) was required to achieve base case SO_2 removal. No significant changes were observed when the Cl^- concentration was increased to 20,000 ppm. However, when the Cl^- concentration was increased to 50,000 and 80,000 ppm, the DBA concentration also had to be raised to 11.3 and 13.0 meq/l, respectively. At 120,000 ppm Cl^-a phenomenon similar to "limestone blinding" was encountered. Ninety percent SO_2 removal efficiency was seldom achieved even though the DBA concentration was increased to 24.7 meq/l (equivalent to 1800 ppm adipic acid). Another effect observed with the increase of calcium chloride concentration was the drop of hold tank pH. Figure 9-4 shows that the hold tank pH dropped from 5.2 to 4.8 when the Cl^- concentration was increased from base case to 80,000 ppm. At 120,000 ppm Cl^-, the average hold tank pH was 4.5. Part of the pH drop was due to the limestone blinding.

9.2 EFFECTS OF CALCIUM CHLORIDE ON DBA DEGRADATION AND COPRECIPITATION RATES

For DBA enhanced limestone scrubbers, the organic acid consumption is due to three important losses during operation:

1. DBA lost in the solution entrained with waste solids

Table 9-3. Operating Conditions for Forced Oxidation DBA Enhanced Limestone Tests

Test	FB-4	FB-5	F2-1A	F5-1A	F8-1A	F12-1A
Cl^- concentration, ppm	Basecase	Basecase	20000	50000	80000	120000
L/G, liter/meter^3	8.3	8.3	7.7	8.3	8.3	8.3
Slurry solids, %	10.6	11.0	11.2	10.8	9.9	10.3
Scrubber feed pH	5.2	5.1	5.2	4.9	4.8	4.5
Scrubber effluent pH	3.0	3.7	3.9	3.8	3.7	3.6
Inlet SO_2, ppm	2420	2520	2400	2490	2460	2450
SO_2 absorption, %	50.2	90.9	90.3	91.6	90.5	87.1
SO_2 make-per-pass, mmole/liter	4.94	9.3	10.1	9.5	9.34	9.0
Limestone stoichiometry	1.08	1.07	1.03	1.02	1.03	1.12
Height of packing, cm	53.3	53.3	53.3	53.3	53.3	53.3
Flue gas O_2, %	5.1	4.7	5.3	5.1	5.1	3.9
Oxidation, %	100	100	100	100	100	95.9
Filter cake solids, %	85.4	86.3	85.7	86.1	86.4	84.3
Slurry settling rate, cm/min	4.3	4.0	4.1	4.3	3.9	3.6
Organic acid concentration, meq/l	0	10.3	10.3	11.3	13.0	24.7
Corresponding adipic acid concentration, ppm	0	750	750	805	950	1800

Table 9-4. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Forced Oxidation DBA Enhanced Limestone Tests

Test	FB-5		F5-1A		F8-1A		F12-1A	
Component, ppm	HT	SE	HT	SE	HT	SE	HT	SE
Ca	1360	1400	31200	31400	42600	41900	65100	67300
Mg	364	391	664	698	803	811	1040	934
Na	68	57	748	744	1210	1310	2000	1930
Cl	1450	1670	48900	50300	79200	80300	122000	119000
SO_3	0	43	0	680	0	712	480	1073
SO_4	1450	1490	832	912	572	633	361	470
CO_3	-	-	82	162	76	-	67	115

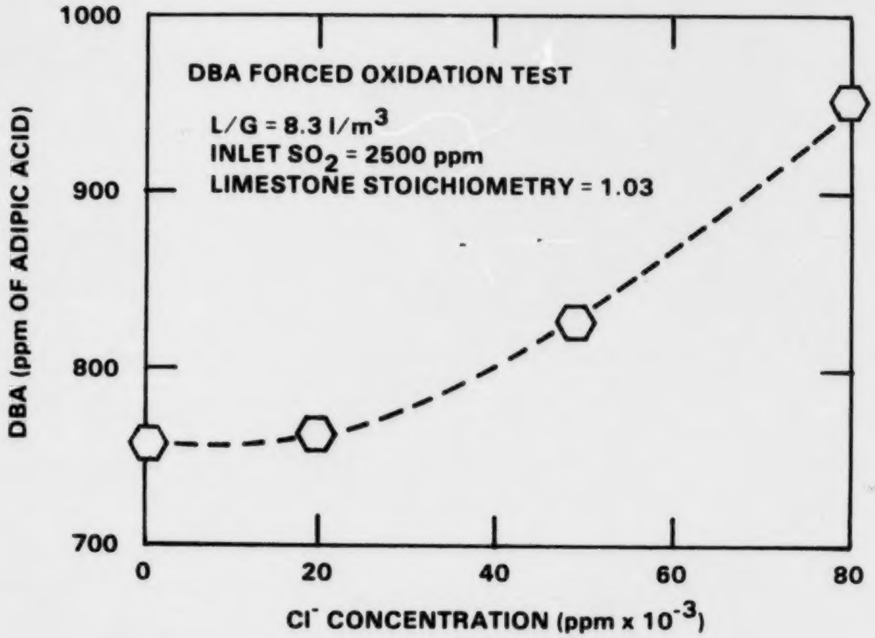


Figure 9-3. DBA required to reach 90% SO_2 removal at high chloride concentrations.

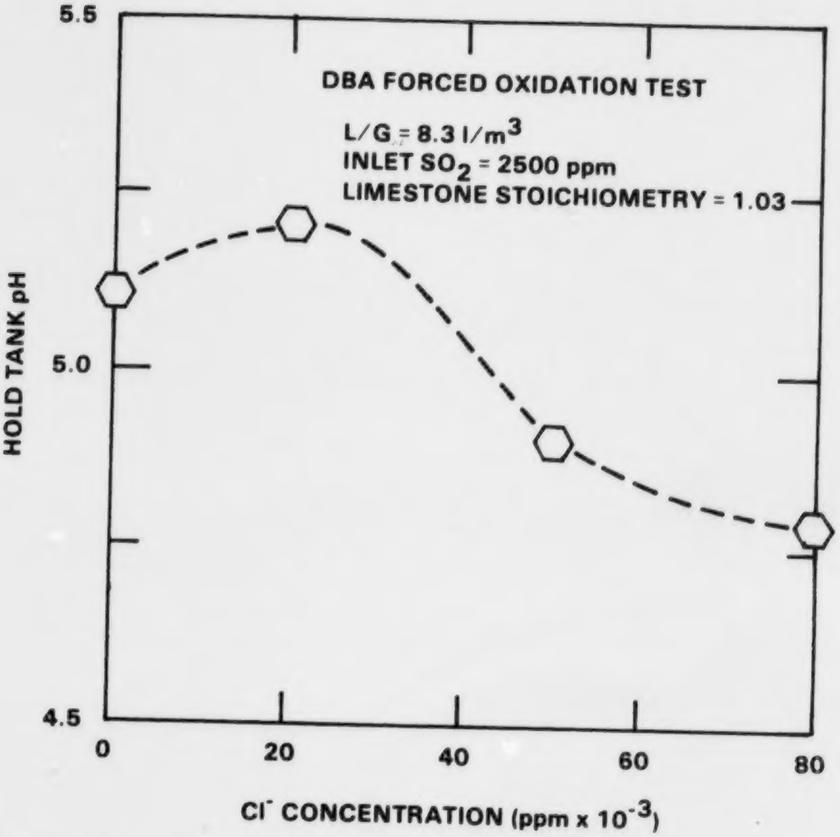


Figure 9-4. Chloride effect on hold tank pH of DBA enhanced limestone scrubber.

2. Organic acids degraded by conjugate oxidation with sulfite

3. DBA coprecipitated with $CaSO_3/SO_4$ solids and lost in the waste solids

The amount of DBA lost as entrained solution varies directly with its concentration in the limestone slurry and with filter cake quality. The organic acid degradation that occurs by reaction with free radicals generated from sulfite oxidation results in decarboxylation of useful organic acid and eventual conversion to "non-active" materials. The coprecipitation rate of organic acid varies inversely as a function of the oxidation rate of sulfite. At oxidation levels less than 10%, the coprecipitation loss could be very signifcant. The sum of degradation and coprecipitation losses is herein referred to as "unaccountable loss". Under forced oxidation conditions, oxidation is usually above 95%, gypsum is produced, and the unaccountable loss is primarily caused by degradation. Under natural oxidation conditions, DBA unaccountable loss is composed of both degradation and coprecipitation.

In order to evaluate the DBA consumption rate at high Cl^- concentrations, long term pilot plant tests were conducted under both natural and forced oxidation conditions. Operating conditions and summaries of scrubbing liquor analyses are shown in Tables 9-5 and 9-6. In order to avoid scaling problems and to sustain long term operation, the Cl^- concentrations were controlled at 30,000 ppm for natural oxidation and 50,000 ppm for forced oxidation tests. The liquid phase organic acid concentrations were measured by silicic acid titration. Sodium (as sodium chloride) was added to the hold tank at a constant rate as a tracer to facilitate estimation of the total liquid discharged. The total liquor discharged included liquid losses through filter cake disposal, scrubber mist eliminator carry-over, sampling, leaks, and other accidental losses. By utilizing sodium as a tracer, the DBA consumption from "normal" scrubber solution losses could be accounted for. The DBA feedrate in excess of the accountable

Table 9-5. Operating Conditions for Long Term DBA Material Balance Tests

Test	N3-4A	F5-4A
Operation mode	Natural Oxidation	Forced Oxidation
Cl^- concentration, ppm	30000	50000
L/G, liter/meter^3	8.5	8.25
Slurry solids, %	10.1	9.9
Scrubber feed pH	4.9	5.5
Scrubber effluent pH	4.4	4.5
Inlet SO_2, ppm	2450	2460
SO_2 absorption, %	93.5	96.5
SO_2 make-per-pass, mmole/liter	10.0	10.1
Limestone stoichiometry	1.11	1.14
Height of packing, cm	53.3	53.3
Flue gas O_2, %	7.4	5.8
Oxidation, %	17.9	98.6
Filter cake solids, %	54	83.5
Organic acid concentration, meq/l	15.1	12.3
Corresponding adipic acid concentration, ppm	1100	900

Table 9-6. Summary of Scrubber Feed (HT) and Scrubber Effluent (SE) Liquor Analysis for Long Term DBA Material Balance Tests

Test	N3-4A		F5-4A	
Component ppm	HT	SE	HT	SE
Ca	9900	10000	24100	24200
Mg	1130	1130	1470	1510
Na	5540	5620	5810	5790
Cl	30800	30800	50100	50300
SO_3	279	919	5	672
SO_4	1240	1010	892	981
CO_3	386	191	121	90

loss was designated as unaccountable loss. As discussed, organic acid degradation and coprecipitation with scrubber solids were the two most likely causes of the unaccountable loss. The data from long term material balance tests can be used to estimate the unaccountable DBA losses at high Cl^- concentrations and to evaluate the effects of Cl^- concentration on DBA degradation and coprecipitation rates.

Results of long term material balance tests are shown in Figures 9-5 and 9-6 for natural oxidation and forced oxidation, respectively. Using the data in Figures 9-5, the sodium balance was made for natural oxidation.

$$Na_{(in)} = Na_{(out,\ in\ liquor\ discharged)} + Na(out,\ in\ solids) \quad (9\text{-}1)$$

$$39.3 = (total\ liquor\ discharged) \cdot (5.5-0.5) + (11.8 \times 454 \times 0.0009) \quad (9\text{-}2)$$

Total liquor discharged = 6.9 l/hr, based on Na (9-3)

The unaccountable DBA loss based on silicic acid analysis and sodium balance was determined as:

In = out + loss (9-4)

$$246 = 15.1 \times 6.9 + loss \quad (9\text{-}5)$$

DBA loss rate = 141.8 meq/hr (equivalent to 10.4 g/hr of adipic acid) (9-6)
under natural oxidation

The sodium balance was made by utilizing data in Figure 9-6.

$$Na_{(in)} = Na_{(out\ in\ liquor\ discharged)} + Na_{(out\ in\ solids)} \quad (9\text{-}7)$$

$$27.5 = (total\ liquor\ discharged) \cdot (5.8-0.5) + (15.24 \times 454 \times 0.0005) \quad (9\text{-}8)$$

Total liquor discharged = 4.53 l/hr, based on Na (9-9)

The unaccountable DBA loss based on silicic acid analysis and sodium balance was determined as:

In = Out + Loss (9-10)

$$246 = 12.3 \times 4.53 + loss \quad (9\text{-}11)$$

DBA loss rate = 190.3 meq/hr (equivalent to 13.9 g/hr of adipic acid) (9-12)

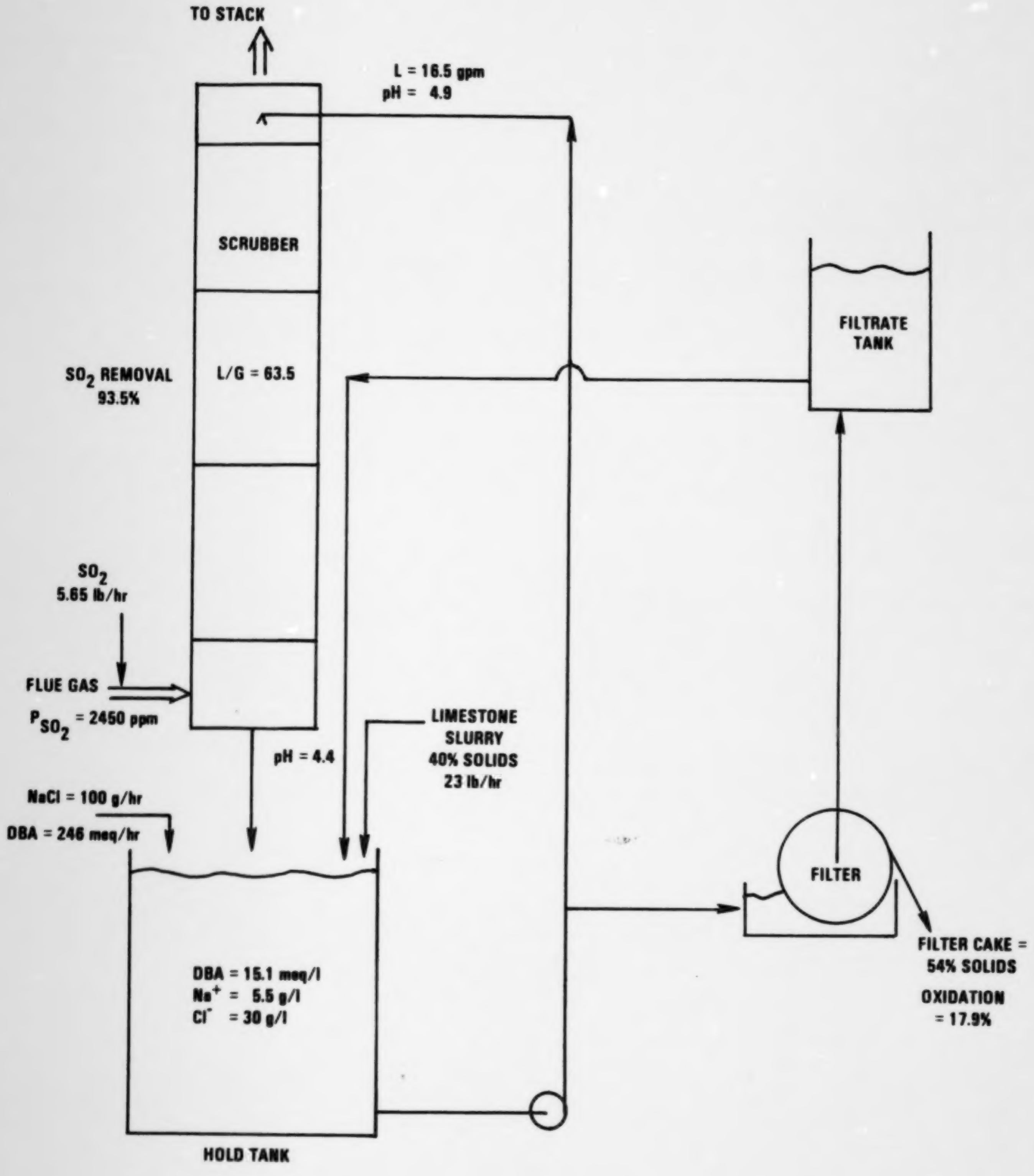


Figure 9-5. Overall material balance for run of N3-4A.

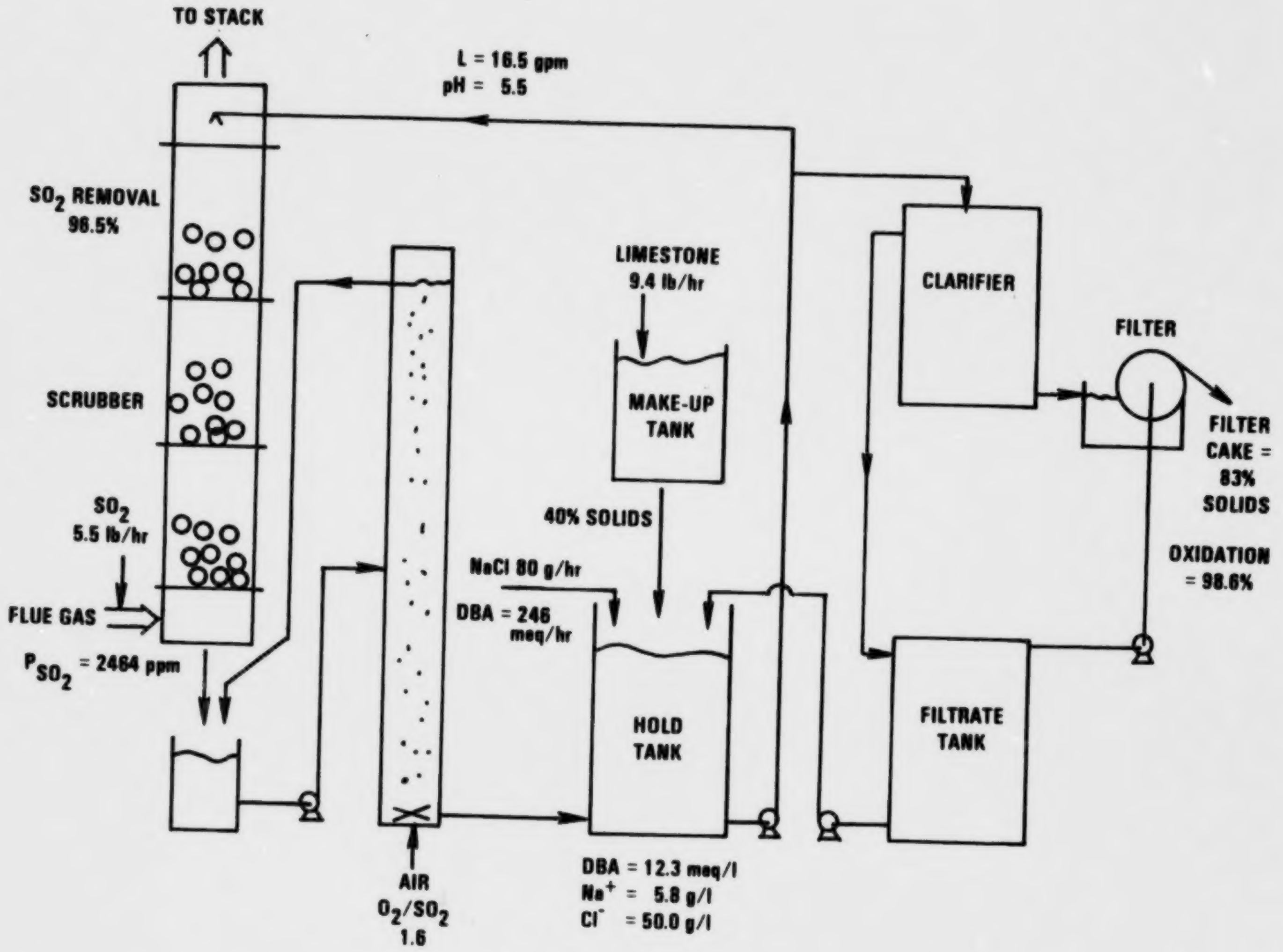


Figure 9-6. Overall material balance for run F5-4A.

The comparison of unaccountable DBA losses at different Cl^- concentrations is shown in Table 9-7. It can be seen that 13.9 g/hr unaccountable DBA loss was obtained at 50,000 ppm Cl^- under forced oxidation conditions which is not significantly different from the loss at Cl- concentration less than 8,000 ppm. Since the unaccountable loss of DBA under forced oxidation is primarily due to degradation, the pilot plant data indicated that DBA degradation rate was not significantly affected by increasing the Cl^- concentration. It is shown in Table 9-7 that under natural oxidation conditions, unaccountable loss of DBA at 30,000 ppm Cl^- was about 35% higher than that at Cl^- concentration below 8,000 ppm. Under natural oxidation conditions, unaccountable DBA loss consists of both degradation and coprecipitation losses. Since forced oxidation data indicated that the DBA degradation rate was not affected by increasing the Cl^- concentration, the increase of unaccountable loss of DBA under natural oxidation was probably due to a higher coprecipitation rate at high Cl^- concentrations. A similar effect of Cl^- on adipic acid coprecipitation rate was also observed by lab-scale experiments at the University of Texas at Austin.

Table 9-7. Comparison of Unaccountable Organic Acid Losses at RTP Limestone FGD Pilot Plant

	Natural Oxidation	Forced Oxidation
Previous data at Cl^- <8,000 ppm	7.4-8 g/hr	14.35 g/hr
Present data at high Cl^- concentration[a]	10.35 g/hr	13.9 g/hr

[a] Cl^- = 30,000 ppm for natural oxidation
Cl^- = 50,000 ppm for forced oxidation

SECTION 10

WASHABILITY EVALUATION OF GYPSUM CAKE PRODUCED FROM HIGH CHLORIDE LIMESTONE SCRUBBING

The use of forced oxidation in FGD systems may be determined by marketability of the resulting gypsum. High concentration of $CaCO_3$ or dissolved salts are unacceptable for wallboard manufacturing (expected to be the largest gypsum market). U.S. wallboard manufacturers have established technical criteria for FGD byproduct gypsum.(27) As shown in Table 10-1, the maximum soluble solids content should be no more than 1800 ppm. The most stringent criteria, as specified by U.S. Gypsum, require chloride concentrations less than 75 ppm and total dissolved solids less than 200 ppm. In order to meet the gypsum specification, filter cake washing is necessary especially with closed-loop operation for which high dissolved solids and high Cl^- concentrations are expected. Relatively pure gypsum is also preferable for cement manufacturing or landfilling.

Pilot plant tests were conducted to demonstrate that gypsum with high purity could be produced from wet limestone FGD with high chloride levels in the process liquor. A belt filter with the capability of three-stage countercurrent washing was utilized to evaluate the washability of dissolved solids from the gypsum cake. Operating parameters evaluated included number of washing stages, amount of wash water, drying time and initial soluble solids contents.

10.1 FILTER MEDIA EVALUATION

The current filter was designed for dewatering unoxidized slurry from a similarly sized dual alkali test facility. In order to dewater gypsum, filter cloth tests were performed to select the appropriate filter media. Five filter cloths made of different weave, thread count, weight, and finish were evaluated. Table 10-2 lists detailed specifications of each cloth. The filter

Table 10-1. Tentative Specification for FGD Byproduct Gypsum by Wallboard Manufacturers(26).

	National Gypsum	Georgia Pacific	U.S. Gypsum
Purity ($CaSO_4 \cdot 2H_2O$)	94% min.	90% min.	95% min.
$CaSO_3$	0.5% max.		2% max.
Na	500 ppm max.	200 ppm max.	75 ppm max.
Cl	800 ppm max.	200 ppm max.	120 ppm max.
Mg	500 ppm max.		50 ppm max.
Free water	10%	10%	10%
Max water	15%		
pH	6.0-8.0	9.0 max 3.0 min	8.0 max. 6.5 min.
Particle size, um			20 min. 40 max.

Table 10-2. Filter Media Evaluated

	EIMCO	EIMCO	EIMCO	EIMCO	AMETEK
Style No.	POPR 852F	POPR 853F	POPR 851	POPR 901F	STE-F9D8-HJ0
Material	pp.(1)	pp.	pp.	pp.	pp.
Weave	2/2 twill	2/2 twill	1/1 twill	2/2 twill	2/2 twill
Yarn	multi-filament	multi-filament	multi-filament	multi-filament	multi-filament
Thread Count	64 x 34	59 x 38	58 x 32	52 x 35	58 x 35
Weight (g/sq meter)	262	255	227	383	255
Finish	Heatset	Heatset	Greige	Heatset	Heatset

(1)polypropylene

cloth evaluation tests were conducted with thickened slurry containing 50,000 ppm Cl^- and 30.9% insoluble solids. Evaluated parameters included filter cake solids content, filtrate solids content, vacuum attained and filtration rate as shown in Table 10-3. It can be seen that significant differences exist between the filter media tested. Eimco filter media style No. POPR-852F was selected as the most applicable of the five tested. It not only generated the highest solids content filter cake but also the lowest solids content filtrate. Good filtration rate was also obtained with reasonable vacuum across the filter bed. It was decided to use Eimco POPR-852F as the filter media for the cake washability tests that followed.

10.2 QUALITY OF GYPSUM EVALUATED

In order to produce high quality (purity) gypsum from the FGD pilot plant, the limestone scrubber was operated with the following features:

- Hold tank pH less than or equal to 5.2 to maximize the limestone utilization (i.e. to minimize the $CaCO_3$ content in the cake)
- DBA enhanced scrubbing to maintain 90% SO_2 removal efficiency
- High Cl^- concentration to simulate closed-loop operation
- Forced oxidation with air flow rate to the oxidizer controlled within the range of 1.5 to 2.0 O_2/SO_2 to obtain complete oxidation of SO_2 absorbed.

Major operating conditions and summaries of test results are shown in Table 9-3, runs F5-1A, F8-1A, and F12-1A. It is seen that at Cl^- concentrations below 80,000 ppm, SO_2 removal efficiency reached 90% and limestone utilization was above 97%. Essentially 100% oxidation was achieved which was reflected by the high filter cake solids content (greater than 86%) and slurry settling rate (greater than 3.9 cm/min). However, phenomena similar to those encountered with "limestone blinding" were observed at

Table 10-3. Results of Filter Media Evaluation Tests

	EIMCO	EIMCO	EIMCO	EIMCO	AMETEK
Style No.	POPR 852F	POPR 853F	POPR 851	POPR 901F	STE-F9D8-HJO
Filter Cake % Solids	84	82	69	57	72
Filtrate % Solids	0.1	0.3	2.4	1.6	1.5
Vacuum Attained, in Hg	10-15	10-15	5	5	5-7
Filtration Rate	good	good	poor	poor	fair

Operating Conditions:

Inlet slurry:	30.9% solids
Slurry feedrate:	5 kg/hr dry cake
Belt speed:	91 cm/min
Chloride conc.:	50,000 ppm

120,000 ppm Cl⁻. System pH dropped significantly. Only 87.1% SO_2 removal efficiency was obtained by increasing the DBA concentration to 24.7 meq/l (equivalent to 1800 ppm adipic acid). Limestone utilization decreased to 89%. The oxidation level also declined to 95.9% even with the increase of air flowrate. Filter cake solids content was 84.3% and slurry settling rate 3.6 cm/min.

10.3 GYPSUM WASHABILITY EVALUATION

Eight filter cake samples were taken at 50,000 ppm Cl^- (slurry concentration) under various filtering and washing conditions as listed in Table 10-4. Results of the cake analyses are shown in Table 10-5. The cake moisture was measured by drying the wet cake in a microwave oven for 10 minutes. The combined water was taken by drying the cake in a convection oven set at 250°C for 24 hours. The concentrations of chloride and water soluble salts were analyzed based on the methods suggested by United States Gypsum Company. Unwashed filter cake samples were taken for Run 0. Table 10-5 shows that the concentrations of chloride and water soluble salts reached 9,330 and 14,500 ppm of cake, respectively. Comparisons of results from Runs 0, 1, 2, 3 and 4 showed the effect of number of displacement washes and Runs 2, 5 and 6 the effect of number of washing stages. (The amount of wash water used is expressed by the number of displacement washes. One displacement means the wash water used is equivalent to the amount of water entrained in the filter cake. Under normal forced oxidation conditions, wash water greater than 5 displacements should be available with closed-loop operation). The data indicates that with 5 displacement washes and 3 stages of countercurrent washing, 99% washing efficiency of Cl^- and water soluble salts was obtained. Results of Run 7 confirmed the 99% washing efficiency data at different filtration rates.

Table 10-4. Summary of Cake Washability Test Conditions With 50,000 ppm Slurry Chloride Concentration
(Run F5-1A)

Run	Number of Washing Stages	Approximate Number of Displacement	Belt Speed cm/min	Approximate Slurry Feedrate, kg/hr dry cake	Fresh Water to Fresh Water Bank l/hr
0	0	0	91	9.1	0
1	3	3	91	9.1	5.3
2	3	5	91	9.1	8.7
3	3	8	91	9.1	14.0
4	3	16	91	9.1	28.0
5	2	5	91	9.1	8.7
6	1	5	91	9.1	8.7
7	3	5	137	13.6	13.2

Table 10-5. Results of Cake Washability Test with 50,000 ppm Slurry Chloride Concentration

Run F5-1A

Slurry Cl:	50,000 ppm
Feed solids:	32.4%
Limestone stoichiometry:	1.0
% SO_2 oxidation:	100%
DBA concentration:	825 ppm

Run	Cake Moisture %	Combined Water %	Cl, ppm	Water Soluble Salts, ppm
0	16.8	19.3	9330	14487.0
1	16.1	16.3	566.0	871.0
2	14.4	21.4	91.0	136.0
3	15.9	19.1	99.0	149.0
4	14.8	21.4	42.0	61.0
5	16.5	18.8	549.0	847.0
6	16.8	19.3	1560	2420
7	14.2	20.3	80.0	121.0

Four filter cake samples were taken at 80,000 ppm Cl^- (slurry concentration) as shown in Table 10-6. The results of cake analyses are listed in Table 10-7. Seven more filter cake samples were taken at 120,000 ppm chloride (slurry concentration) (Table 10-8). Due to mechanical problems with the wash water recycle pump, the washing was limited to two stages. However, Table 10-9 indicates that 98% washing efficiencies were reached for both chloride and water soluble salts.

The washing efficiency of countercurrent washing with complete mixing at each stage can be calculated by

$$\text{washing efficiency} = \left(1 - \frac{R - 1}{R^{m+1} - 1}\right) \times 100\% \qquad (10\text{-}1)$$

where R is the number of wash displacements and m the number of washing stages. Figure 10-1 shows the comparison of cake washing efficiencies between RTP data and theoretical predictions from equation (10-1). Good agreement was obtained. Table 10-10 compares the RTP filter cake qualities with the gypsum qualities specified by United States Gypsum Company for wallboard manufacturing. It is seen that with 3-stage countercurrent washing and 5 displacement washes, filter cakes from slurries with 50,000 ppm and 80,000 ppm Cl^- could meet all the requirements for wallboard manufacturing. With 2-stage countercurrent washing and 5 displacement washes, the filter cake chloride concentration from the slurry with 120,000 ppm Cl^- was slightly higher than the required limit. Due to the operation problem with "limestone blinding", the $CaSO_3 \cdot 1/2\ H_2O$ and $CaCO_3$ contents were also higher than the required gypsum qualities.

Table 10-6. Summary of Cake Washability Test Conditions with Slurry Chloride Concentration at 80,000 ppm (Run F8-1A)

Run	Number of Washing Stages	Approximate Number of Displacement	Belt Speed cm/min	Approximate Slurry Feedrate, kg/hr dry cake	Fresh Water to Fresh Water Bank l/hr
0	0	0	91	9.1	0
1	3	5	91	9.1	8.7
2	2	5	91	9.1	8.7
3	1	5	91	9.1	8.7

Table 10-7. Results of Cake Washability Test With 80,000 ppm Slurry Chloride Concentration

Run F8-1A	
Slurry Cl:	80,000 ppm
Feed solids:	30.6%
Limestone stoichiometry:	1.0
% SO_2 oxidation:	100%
DBA concentration:	950 ppm

Run	Cake Moisture %	Combined Water %	Cl, ppm	Water Soluble Salts, ppm
0	13.9	20.2	14800	23100
1	15.4	19.6	98.6	148
2	14.3	21.5	371	573
3	14.6	19.6	2240	3480

Table 10-8. Summary of Cake Washability Test Conditions with 120,000 ppm Slurry Chloride Concentration (Run F12-1A)

Run	Number of Washing Stages	Approximate Number of Displacement	Belt Speed cm/min	Approximate Slurry Feedrate, kg/hr dry cake	Fresh Water to Fresh Water Bank l/hr
0	0	0	91	9.1	0
1	2	5	91	9.1	8.7
2	1	5	91	9.1	8.7
3	2	3	182	18.2	10.6
4	2	5	182	18.2	17.4
5	2	10	182	18.2	34.8
6*	2	10	182	18.2	34.8

*All three sprays fresh water

Table 10-9. Results of Cake Washability Test With 120,000 ppm Slurry Chloride Concentration

Run F12-1A

Slurry Cl:	120,000 ppm
Feed solids:	32.5%
Limestone stoichiometry:	1.1
% SO_2 oxidation:	95.9%
DBA concentration:	1800 ppm

Run	Cake Moisture %	Combined Water %	Cl, ppm	Water Soluble Salts, ppm
0	13.7	21.2	20900	32600
1	16.8	20.3	292	452
2	15.7	20.7	4520	7060
3	18.7	19.4	1200	1870
4	17.5	19.6	355	550
5	14.6	20.7	372	575
6	14.1	20.4	163	250

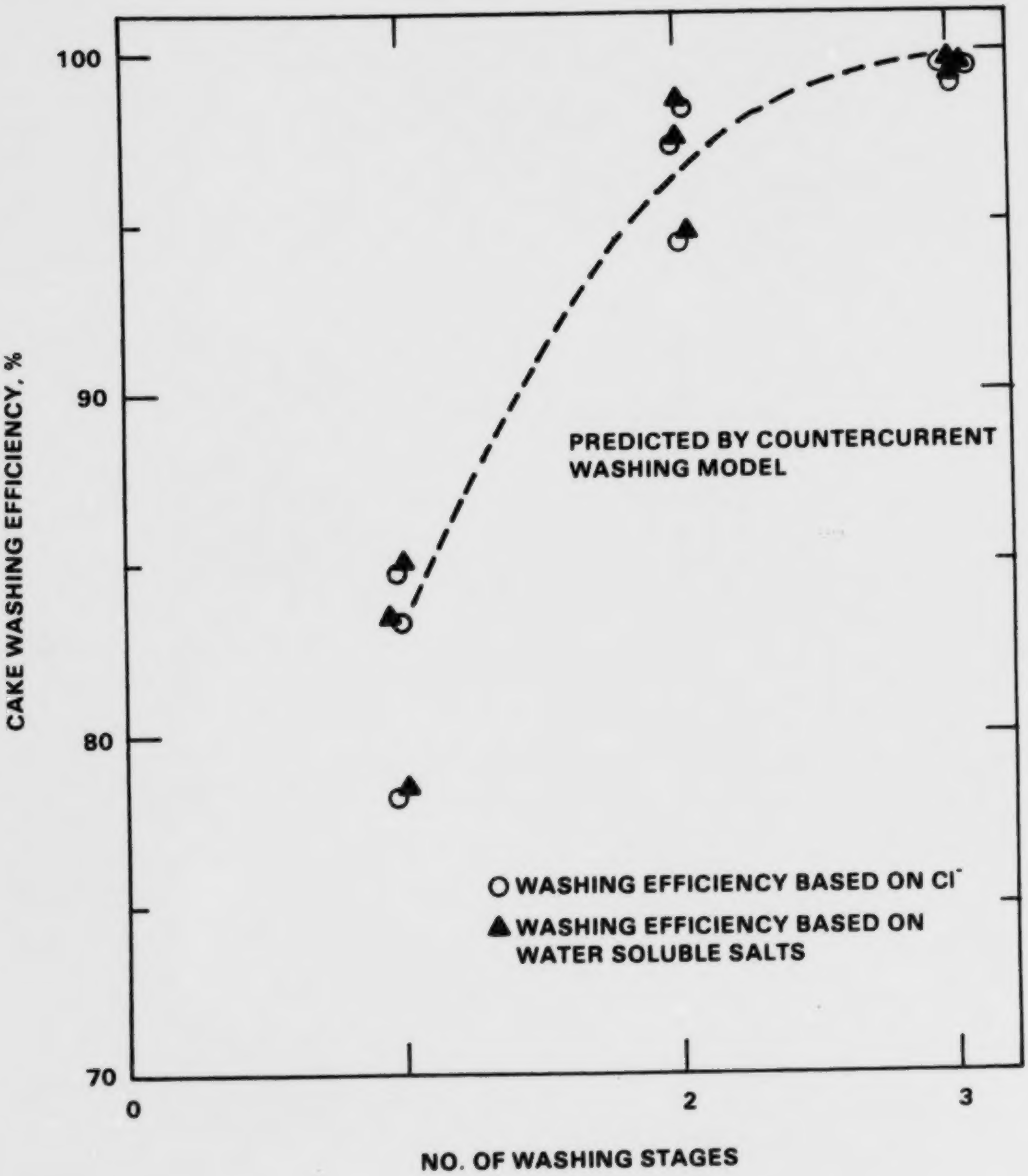


Figure 10-1. Performance of belt filter counter-current washing at 5 wash displacement water.

Table 10-10. Comparison of Gypsum Qualities

	Required[a] Quality	RTP Sample[b] from slurry with 50,000 ppm Cl (Run F5-1A)	RTP Sample[b] from slurry with 80,000 ppm Cl (Run F-8-1A)	RTP Sample[c] from slurry with 120,000 ppm Cl (Run F12-1A)
Free water, % (dried at 43.3°C)	<10	14.4	15.4	15.7
Combined water, % (dried at 250°C)	>19.8	21.4	19.6	20.7
$CaSO_3 \cdot 1/2\ H_2O$, %	<2	<1	<1	2.1
$CaCO_3$, %	<2	<1	<1	3.7
CaO, %	31~33	32.6	32.6	33.8
SO_3, %	>44	46.1	45.9	45.0
Na, ppm	<75	<5	<5	<5
K, ppm	<75	<5	<5	<5
Mg, ppm	<50	8.0	6.0	8.0
Cl, ppm	<120	90.6	98.6	292
Total water soluble salts, ppm	<600	136	148	452

[a] specified by United States Gypsum Company for wallboard

[b] washed by 5 displacement water with 3-stage-countercurrent washing

[c] washed by 5 displacement water with 2-stage-countercurrent washing

NOTATION
(All Sections)

a = surface area of gas-liquid interface per unit volume of absorber, cm^{-1}

A = component activity, gmole/liter

C = component concentration, gmole/liter

C' = correlation constant in Equation (4-20)

D = component diffusivity, cm^2/sec

G = gas flow rate, gmole/sec-cm^2

I = ionic strength, gmole/liter

K_G = overall gas-phase mass transfer coefficient, gmole/sec-atm-cm^2

k_g = gas-phase mass transfer coefficient, gmole/sec-atm-cm^2

k_l = liquid-phase mass transfer coefficient, liter/sec-cm^2

K_{sp} = solubility product, $(gmole/liter)^2$

K = equilibrium constant

m = number of washing stages

n = ionic valence

N = molar flux, gmole/sec-cm^2

P = partial pressure, atm

P_T = total pressure, atm

r = dimensionless parameter in Equation (4-18)

R = number of wash displacement

Z = total height of the absorbing section, cm

α = parameter in Equation (4-4), gmole/liter-atm

ϕ = mass transfer enhancement factor

Subscript

A = alkalinity

b = base case

h = high chloride case

j = j^th component

w = water

Superscript

i = gas-liquid interphase

o = bulk liquid

x = correlation parameter in Equation (4-20)

y = correlation parameter in Equation (4-20)

z = correlation parameter in Equation (4-21)

REFERENCES
(All Sections)

(1) Hargrove, O.W., "The Effects of Process Water Selection on Lime-Limestone Flue Gas Desulfurization Chemistry", Electric Power Research Institute Report CS-2451, July, 1982.

(2) Rao, R., and R. Salib, "Designing a Flue Gas Desulfurization System for Worst Case Operating Conditions", Presented at the Air Pollution Control Association Annual Meeting, June 1982.

(3) Evers, R., V. E. Vandergriff, R. L. Zielke, "Field Study to Obtain Trace Element Mass Balances at a Coal-fired Utility Boiler", EPA-600/7-80-171, October, 1980.

(4) Personal Communication with B. Laseke, PEDCo Environmental, March 1, 1982 by D. Laslo.

(5) PEDCo Environmental, Inc., "Survey of Design and Actual Chloride Levels in Commercial Closed Water Loop FGD System", Prepared under contract for Peabody Process Systems, Inc., unpublished, Feb, 1982.

(6) Head, H., "EPA Alkali Scrubbing Test Facility: Advanced Program, Third Progress Report", EPA-600/7-77-105, September, 1977.

(7) Burbank, D. A., S. C. Wang, "EPA Alkali Scrubbing Test Facility: Advanced Program - Final Report (October 1974 - June 1978)," EPA-600/7-80-115, May, 1980.

(8) Borgwardt, R. H., "Effect of Forced Oxidation on Limestone/SO_x Scrubber Performance", Preceedings: Symposium on Flue Gas Desulfurization, Hollywood, FL, EPA 600-7-78-058a, p205, 1978.

(9) Rochelle, G., "Limestone Dissolution in Aqueous Solution," EPA Grant R806351, Monthly Progress Report, June, 1981.

(10) Furuta, I., "Desulfurization Process," United States Patent 3,959,441, May 25, 1976.

(11) Borgwardt, R. H., "Combined Flue Gas Desulfurization and Water Treatment in Coal Fired Power Plants", Environmental Science & Technology, Vol. 14, No. 3, p 294-298, March, 1980.

(12) Rader, P. C., R. W. Hanson, D. C. Borsare, "Design of Lime/Limestone Flue Gas Desulfurization Systems for High Chlorides". Presented at Coal Technology '81, Houston, TX, November, 1981.

(13) Personal communication with P. Rader by D. Laslo on 11/20/81.

(14) Morris, K., "Methods of Air Sampling and Analysis", 2nd Ed, p737, American Public Health Association, 1977.

(15) Rochelle, G. T., and C. J. King, "The Effect of Additives on Mass Transfer in $CaCO_3$ or CaO Slurry Scrubbing of SO_2 From Waste Gases", Ind. Eng. Chem. Fund., 16, 67, 1977.

(16) Onda, K., E. Sada, T. Kobayaski, S. Kito, and K. Ito, "Salting-Out Parameters of Gas Solubility in Aqueous Salt Solutions", Journal of Chemical Engineering of Japan, 3, 1, 18, 1970.

(17) Ratcliff, G. A., and J. G. Holdcroft, "Diffusivities of Gases in Aqueous Electrolyte Solutions", Trans. Inst. Chem. Engrs., 41, 315, 1963.

(18) Chang, C. S., and G. T. Rochelle, "SO_2 Absorption into Aqueous Solutions," AIChE Journal, 27, 2, 292, 1981

(19) Hatfield, J. D., and A. V. Slack, "Sulfur Removal and Recovery from Industrial Processes", Advances in Chemistry Series 139, American Chemical Society, p. 130, 1975.

(20) Lowell, P. S., D. M. Ottmers, K. Schwitzgebel, T. I. Strange, and D. W. Deberry, P. G. 193-029, U.S. Environmental Protection Agency, 1970.

(21) Epstein, M., "EPA Alkali Scrubbing Test Facility: Summary of Testing Through October 1974," NTIS PB-244901/AS, June 1975.

(22) Wang, S.C., and D. Burbank, "Adipic Acid Enhanced Lime and Limestone Testing at the EPA Alkali Scrubbing Test Facility - Final Report," NTIS PB 82-230624, March 1982.

(23) Rader, P. C., D. C. Borio, S. L. Goodstine and M. R. Gogineni, "The Role of Crystallization in the Design of Lime/Limestone Wet Scrubbing Systems for Flue Gas Desulfurization", Presented at the 83rd National AIChE Meeting in Houston, March, 1977.

(24) Mobley, J. D. and C. S. Chang, "The Adipic Acid Enhanced Limestone Flue Gas Desulfurization Process, An Assessment", JAPCA, 31, 12, 1249, 1981.

(25) Chang, C. S., and g. T. Rochelle, "Effect of Organic Acid Additives on SO_2 Absorption into $CaO/CaCO_3$ Slurries," AIChE Journal, 28, 2, 261, 1982.

(26) Chang, C. S., and J. D. Mobley, "Testing and Commercialization of Byproduct Dibasic Acids as Buffer Additives for Limestone Flue Gas Desulfurization Systems," JAPCA, 33, 10, 1983.

(27) Goodwin, R.W., "Resource Recovery from Flue Gas Desulfurization Systems," JAPCA, 32, 9, 986, 1982.

APPENDIX A

DATABASE TABLES OF TEST RESULTS

Test Identification Number	NB-1	N2-1	N2-2	N3-1	N3-2
Test Duration, hours	67	72	10	75	12
Date	9/14/81	9/28/81	10/1/81	10/5/81	10/8/81
Cl Concentration, mg/l	167.0	20500.0	20500.0	31400.0	31400.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	10.1	9.7	10.1	9.9	9.9
Scrubber Feed pH	6.0	5.3	5.4	5.2	5.4
Scrubber Effluent pH	5.6	4.9	5.2	4.9	5.1
SO_2 Inlet Conc., PPM	2565.0	2565.0	2565.0	2565.0	2565.0
SO_2 Removal Efficiency, %	79.0	73.0	80.0	70.0	79.0
SO_2 Make-per-pass, mM	8.4	7.8	8.4	7.5	8.4
Limestone Utilization, %	80.0	76.4	50.0	74.6	39.0
Filter Cake Solids Conc., w%	53.0	47.0	50.0	49.0	51.0
Solids Settling Rate, cm/min	0.5	0.3	0.5	0.3	0.6
Gypsum Saturation Feed, %	50.2	89.9	-	94.1	-
Gypsum Saturation Effluent, %	67.7	131.8	-	134.9	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	10.4	9.8	10.0	9.1	11.2
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	N4-1	N4-2	N4-3	N5-1	N4-3A
Test Duration, hours	55	10	71	87	9
Date	10/12/81	10/16/81	10/19/81	11/2/81	10/22/81
Cl Concentration, mg/l	40530.0	40530.0	40730.0	50100.0	41500.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	5.3
Feed Solids Conc., w%	10.1	9.8	14.8	10.4	-
Scrubber Feed pH	5.1	5.2	5.0	4.9	-
Scrubber Effluent pH	4.6	5.0	4.5	4.5	-
SO_2 Inlet Conc., PPM	2611.0	2656.0	2611.0	2565.0	2669.0
SO_2 Removal Efficiency, %	62.0	81.0	66.0	58.0	48.0
SO_2 Make-per-pass, mM	6.7	9.1	7.2	6.2	8.0
Limestone Utilization, %	72.4	32.8	75.5	71.5	-
Filter Cake Solids Conc., w%	52.0	57.0	51.5	52.3	-
Solids Settling Rate, cm/min	0.3	0.4	0.2	0.2	-
Gypsum Saturation Feed, %	116.9	-	85.1	115.6	-
Gypsum Saturation Effluent, %	171.0	-	92.5	139.5	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	11.3	11.8	11.3	9.5	-
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	N4-3B	N4-3C	N5-2	N5-3	N5-4
Test Duration, hours	11	9	23	18	19
Date	10/22/81	10/23/81	11/23/81	11/24/81	11/24/81
Cl Concentration, mg/l	41500.0	41500.0	50000.0	50000.0	50000.0
L/G, l/cu. M	10.7	13.4	5.3	10.7	13.4
Feed Solids Conc., w%	-	-	14.9	14.3	14.5
Scrubber Feed pH	-	-	5.0	5.1	5.0
Scrubber Effluent pH	-	-	4.3	4.4	4.7
SO_2 Inlet Conc., PPM	2630.0	2677.0	2524.0	2476.0	2429.0
SO_2 Removal Efficiency, %	72.0	76.0	43.6	69.6	75.5
SO_2 Make-per-pass, mM	5.9	5.1	6.8	5.4	4.7
Limestone Utilization, %	-	-	80.0	74.1	71.0
Filter Cake Solids Conc., w%	-	-	-	-	-
Solids Settling Rate, cm/min	-	-	0.2	0.2	0.2
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	-	-	10.4	10.1	10.8
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	N10-1	N10-2	N5-1A	N5-2A	N5-3A
Test Duration, hours	62	16	42	72	55
Date	11/30/81	12/4/81	12/8/81	12/10/81	12/17/81
Cl Concentration, mg/l	101600.0	98000.0	50300.0	50800.0	50100.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	10.6	11.6	10.1	10.0	10.1
Scrubber Feed pH	4.6	4.9	4.9	5.1	5.1
Scrubber Effluent pH	4.0	4.6	4.4	4.5	4.6
SO_2 Inlet Conc., PPM	2513.0	2442.0	2497.0	2513.0	2525.0
SO_2 Removal Efficiency, %	32.7	72.4	70.1	80.2	88.2
SO_2 Make-per-pass, mM	3.4	7.5	7.4	8.5	9.3
Limestone Utilization, %	74.7	15.9	69.7	72.6	73.9
Filter Cake Solids Conc., w%	50.9	55.8	52.9	55.0	52.0
Solids Settling Rate, cm/min	0.2	0.3	0.2	0.2	0.2
Gypsum Saturation Feed, %	96.0	-	-	-	-
Gypsum Saturation Effluent, %	137.6	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	424.0	650.0	928.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	10.3	10.0	9.9	9.9	9.6
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	NA-1	NA-2	NA-3	NA-4	N5-5
Test Duration, hours	18	16	15	17	22
Date	12/28/81	12/29/81	12/29/81	12/30/81	1/4/82
Cl Concentration, mg/l	3000.0	3000.0	3000.0	3000.0	50000.0
L/G, l/cu. M	7.9	7.9	4.8	2.4	8.0
Feed Solids Conc., w%	14.3	14.6	14.5	14.4	9.3
Scrubber Feed pH	5.8	5.8	5.7	5.7	5.0
Scrubber Effluent pH	5.6	5.7	5.5	5.6	4.6
SO_2 Inlet Conc., PPM	1736.0	907.0	1724.0	1647.0	1530.0
SO_2 Removal Efficiency, %	85.2	93.7	71.2	62.7	65.9
SO_2 Make-per-pass, mM	6.6	3.8	9.0	16.2	4.3
Limestone Utilization, %	46.5	53.7	43.2	37.3	73.0
Filter Cake Solids Conc., w%	58.7	61.1	62.3	62.8	60.7
Solids Settling Rate, cm/min	-	-	-	-	0.1
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	9.6	9.7	9.3	9.5	9.1
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	N5-6	N5-7	N5-8	NB-3	NB-4
Test Duration, hours	29	29	18	16	14
Date	1/5/82	1/6/82	1/7/82	1/11/82	1/12/82
Cl Concentration, mg/l	50000.0	50000.0	50000.0	0.0	0.0
L/G, l/cu. M	8.0	8.0	8.0	5.3	10.7
Feed Solids Conc., w%	10.0	9.4	9.7	9.7	9.5
Scrubber Feed pH	4.8	4.6	4.6	5.9	5.8
Scrubber Effluent pH	4.3	4.1	4.1	5.4	5.3
SO_2 Inlet Conc., PPM	2460.0	523.0	518.0	2450.0	2515.0
SO_2 Removal Efficiency, %	55.3	73.8	71.2	67.3	86.8
SO_2 Make-per-pass, mM	5.8	1.7	1.6	10.4	6.9
Limestone Utilization, %	81.0	69.0	83.0	71.0	71.0
Filter Cake Solids Conc., w%	54.4	52.0	53.1	61.8	61.3
Solids Settling Rate, cm/min	0.2	0.2	0.2	0.4	0.5
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	8.6	8.7	8.8	11.4	11.2
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	NB-5	NB-6	NB-7	NL-1	NL-2
Test Duration, hours	11	26	28	15	20
Date	1/12/82	1/18/82	1/20/82	2/23/82	2/24/82
Cl Concentration, mg/l	0.0	0.0	0.0	0.0	0.0
L/G, l/cu. M	13.2	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	9.8	9.7	9.7	10.1	9.6
Scrubber Feed pH	5.8	5.4	5.8	4.0	3.7
Scrubber Effluent pH	5.5	5.0	5.5	3.9	3.0
SO_2 Inlet Conc., PPM	2475.0	2436.0	493.0	2485.0	2531.0
SO_2 Removal Efficiency, %	89.7	69.3	91.2	13.3	25.2
SO_2 Make-per-pass, mM	5.6	7.0	1.9	1.4	2.8
Limestone Utilization, %	71.0	97.0	71.0	94.6	91.7
Filter Cake Solids Conc., w%	61.9	62.3	65.3	-	-
Solids Settling Rate, cm/min	0.5	0.5	0.5	-	-
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	11.1	9.7	10.2	10.4	10.6
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	NL-3	NN-1	NN-2	N1-1	N1-2
Test Duration, hours	9	30	25	20	21
Date	2/25/82	3/2/82	3/3/82	3/9/82	3/10/82
Cl Concentration, mg/l	0.0	25000.0	50000.0	10000.0	15000.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	9.9	10.0	10.0	10.2	9.8
Scrubber Feed pH	3.8	5.9	5.2	5.6	5.5
Scrubber Effluent pH	2.5	5.5	4.8	5.0	4.9
SO_2 Inlet Conc., PPM	1006.0	2503.0	2514.0	2501.0	2484.0
SO_2 Removal Efficiency, %	60.9	79.0	72.0	76.0	73.7
SO_2 Make-per-pass, mM	2.6	8.4	7.6	8.1	8.0
Limestone Utilization, %	97.0	72.0	70.0	72.3	74.5
Filter Cake Solids Conc., w%	-	57.0	59.0	60.0	63.0
Solids Settling Rate, cm/min	-	-	-	0.6	0.6
Gypsum Saturation Feed, %	-	27.4	124.1	121.1	-
Gypsum Saturation Effluent, %	-	30.5	169.4	155.7	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	11.2	10.3	10.5	10.4	10.4
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	NB-8	NB-9	NB-10	NB-11	N5-LM1
Test Duration, hours	21	33	47	33	48
Date	3/16/82	3/18/82	3/23/82	3/25/82	3/29/82
Cl Concentration, mg/l	0.0	0.0	0.0	0.0	50000.0
L/G, l/cu. M	11.2	7.2	10.7	4.5	10.7
Feed Solids Conc., w%	9.7	10.0	9.6	9.7	10.1
Scrubber Feed pH	5.8	5.9	5.8	5.9	4.9
Scrubber Effluent pH	5.5	5.5	5.4	5.5	4.4
SO_2 Inlet Conc., PPM	2448.0	483.0	2496.0	493.0	2513.0
SO_2 Removal Efficiency, %	89.3	92.0	56.3	52.3	47.4
SO_2 Make-per-pass, mM	7.7	2.3	4.5	1.9	3.9
Limestone Utilization, %	85.2	87.8	83.8	81.7	90.0
Filter Cake Solids Conc., w%	61.6	-	60.8	-	69.4
Solids Settling Rate, cm/min	0.6	0.6	0.6	0.6	0.6
Gypsum Saturation Feed, %	-	58.8	88.7	-	131.5
Gypsum Saturation Effluent, %	-	63.5	100.8	-	195.8
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	10.9	10.1	10.7	10.6	11.0
Height Packing, cm	53.3	64.8	0.0	0.0	0.0

Test Identification Number	N5-LM2	N5-LM3	N5-LM4	N5-HM1	N5-HM2
Test Duration, hours	18	38	21	41	16
Date	4/1/82	4/5/82	4/8/82	4/12/82	4/14/82
Cl Concentration, mg/l	50000.0	50000.0	50000.0	50000.0	50000.0
L/G, l/cu. M	10.7	4.7	4.7	11.2	11.2
Feed Solids Conc., w%	10.2	10.3	10.1	10.2	10.3
Scrubber Feed pH	5.2	5.4	5.8	5.0	5.2
Scrubber Effluent pH	4.7	5.1	5.6	4.5	4.7
SO_2 Inlet Conc., PPM	2492.0	515.0	508.0	2517.0	2507.0
SO_2 Removal Efficiency, %	56.9	42.7	55.3	81.1	90.0
SO_2 Make-per-pass, mM	4.7	1.5	2.0	6.7	7.4
Limestone Utilization, %	52.0	80.0	47.5	85.9	63.1
Filter Cake Solids Conc., w%	-	68.7	-	59.3	-
Solids Settling Rate, cm/min	-	0.5	-	0.5	-
Gypsum Saturation Feed, %	-	137.3	-	132.8	-
Gypsum Saturation Effluent, %	-	157.2	-	202.7	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	11.0	10.8	10.8	11.2	11.2
Height Packing, cm	0.0	0.0	0.0	64.8	64.8

Test Identification Number	N5-HM3	N5-HM4	NS-1	NS-2	NS-3
Test Duration, hours	42	19	44	18	17
Date	4/19/82	4/22/82	4/26/82	4/28/82	4/29/82
Cl Concentration, mg/l	50000.0	50000.0	0.0	0.0	0.0
L/G, l/cu. M	7.2	7.2	8.6	8.4	8.4
Feed Solids Conc., w%	9.8	10.1	3.2	6.5	9.6
Scrubber Feed pH	5.1	5.4	5.8	5.8	5.8
Scrubber Effluent pH	4.7	5.2	5.4	5.4	5.4
SO_2 Inlet Conc., PPM	512.0	510.0	2543.0	2512.0	2491.0
SO_2 Removal Efficiency, %	84.2	91.1	75.2	80.4	82.2
SO_2 Make-per-pass, mM	2.1	2.2	9.1	9.7	10.0
Limestone Utilization, %	82.7	43.0	66.6	71.9	77.2
Filter Cake Solids Conc., w%	83.7	-	53.2	60.1	65.5
Solids Settling Rate, cm/min	0.5	-	0.5	0.6	0.4
Gypsum Saturation Feed, %	125.8	-	-	-	-
Gypsum Saturation Effluent, %	155.5	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	10.4	10.4	9.9	9.4	9.5
Height Packing, cm	64.8	64.8	-	-	-

Test Identification Number	NS-4	NS-5	NN-3	N2-3	N3-3
Test Duration, hours	16	31	55	18	17
Date	5/4/82	5/5/82	6/14/82	8/17/82	8/18/82
Cl Concentration, mg/l	50000.0	50000.0	50000.0	20000.0	30000.0
L/G, l/cu. M	8.6	8.6	8.0	8.0	8.0
Feed Solids Conc., w%	10.3	3.4	9.7	9.9	9.8
Scrubber Feed pH	5.1	4.9	5.9	5.2	5.2
Scrubber Effluent pH	4.7	5.0	5.6	4.6	4.6
SO_2 Inlet Conc., PPM	2487.0	2478.0	2483.0	2475.0	2614.0
SO_2 Removal Efficiency, %	77.5	69.8	79.3	72.9	71.5
SO_2 Make-per-pass, mM	9.2	8.3	8.8	7.7	7.6
Limestone Utilization, %	68.9	60.4	74.9	74.6	74.4
Filter Cake Solids Conc., w%	54.8	48.6	58.8	-	52.5
Solids Settling Rate, cm/min	0.2	0.4	0.4	0.5	0.4
Gypsum Saturation Feed, %	-	-	36.7	72.7	-
Gypsum Saturation Effluent, %	-	-	38.6	102.0	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	9.4	8.7	10.6	4.6	5.8
Height Packing, cm	-	-	-	-	-

Test Identification Number	N10-3	NN-4	NN-5	NB-1A	N2-1A
Test Duration, hours	36	47	26	52	42
Date	8/19/82	8/23/82	8/25/82	11/8/82	11/10/82
Cl Concentration, mg/l	100000.0	110000.0	80000.0	0.0	20000.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	10.0	9.4	9.6	9.9	10.2
Scrubber Feed pH	4.8	5.4	5.6	6.0	5.4
Scrubber Effluent pH	4.1	5.1	5.2	5.6	4.9
SO_2 Inlet Conc., PPM	2478.0	2547.0	2503.0	2575.0	2560.0
SO_2 Removal Efficiency, %	48.0	61.5	70.7	80.2	81.2
SO_2 Make-per-pass, mM	4.9	6.3	7.1	8.5	8.7
Limestone Utilization, %	71.0	81.0	81.3	76.3	77.2
Filter Cake Solids Conc., w%	49.5	51.3	52.5	54.5	55.6
Solids Settling Rate, cm/min	0.2	0.6	0.6	0.5	0.5
Gypsum Saturation Feed, %	-	-	60.6	-	-
Gypsum Saturation Effluent, %	-	-	66.2	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	241.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	6.0	5.5	5.5	5.6	5.8
Height Packing, cm	-	-	-	-	-

Test Identification Number	N5-4A	N8-1A	NB-11A	NB-5A	N2-2A
Test Duration, hours	48	46	34	67	53
Date	11/5/82	11/17/82	2/8/83	2/15/83	2/22/83
Cl Concentration, mg/l	50000.0	80000.0	0.0	0.0	20000.0
L/G, l/cu. M	8.0	8.0	8.3	8.3	8.3
Feed Solids Conc., w%	10.3	9.8	9.8	9.5	9.8
Scrubber Feed pH	5.0	4.8	5.2	5.2	5.1
Scrubber Effluent pH	4.5	4.3	4.6	4.6	4.6
SO_2 Inlet Conc., PPM	2510.0	2540.0	23520.0	2518.0	2482.0
SO_2 Removal Efficiency, %	81.0	81.0	49.5	90.7	90.1
SO_2 Make-per-pass, mM	8.6	8.6	5.3	9.9	9.3
Limestone Utilization, %	77.0	77.0	83.3	92.3	92.6
Filter Cake Solids Conc., w%	56.2	54.3	53.6	54.5	54.7
Solids Settling Rate, cm/min	0.5	0.4	0.5	0.5	0.5
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	526.0	672.0	0.0	781.0	883.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	5.5	5.7	7.3	7.0	7.2
Height Packing, cm	-	-	-	-	-

Test Identification Number	N5-5A	N8-2A	N5-6A	N3-2A	N3-3A
Test Duration, hours	49	78	67	28	65
Date	2/28/83	3/7/83	3/14/83	3/23/83	3/28/83
Cl Concentration, mg/l	50000.0	80000.0	50000.0	30000.0	30000.0
L/G, l/cu. M	8.3	8.2	8.1	8.1	8.3
Feed Solids Conc., w%	9.6	11.7	10.1	10.0	10.5
Scrubber Feed pH	4.7	4.4	4.7	5.2	4.9
Scrubber Effluent pH	4.2	3.9	4.2	4.6	4.4
SO_2 Inlet Conc., PPM	2519.0	2465.0	2493.0	2465.0	2481.0
SO_2 Removal Efficiency, %	89.7	81.8	90.8	92.5	94.1
SO_2 Make-per-pass, mM	9.1	8.6	9.7	10.0	10.0
Limestone Utilization, %	93.0	83.3	94.2	88.0	90.0
Filter Cake Solids Conc., w%	55.4	55.3	53.4	54.7	54.2
Solids Settling Rate, cm/min	0.4	0.3	0.4	0.7	0.4
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	1080.0	2131.0	1117.0	760.0	1124.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	7.1	7.4	7.6	6.4	6.3
Height Packing, cm	-	-	-	-	-

Test Identification Number	FB-1	FB-2	FB-3	F2-1	F5-1
Test Duration, hours	59	43	33	21	56
Date	9/21/81	9/23/81	1/22/82	1/25/82	1/26/82
Cl Concentration, mg/l	124.0	130.0	0.0	-	50200.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	10.4	8.8	9.4	10.5	10.1
Scrubber Feed pH	6.6	7.1	5.9	5.8	5.7
Scrubber Effluent pH	5.7	6.3	5.1	4.9	4.6
SO_2 Inlet Conc., PPM	2475.0	548.0	2470.0	2330.0	2456.0
SO_2 Removal Efficiency, %	84.0	93.0	80.3	78.8	72.8
SO_2 Make-per-pass, mM	8.7	2.1	8.4	8.1	7.7
Limestone Utilization, %	82.2	84.0	86.0	85.0	82.0
Filter Cake Solids Conc., w%	73.0	85.0	78.2	78.6	77.2
Solids Settling Rate, cm/min	3.1	4.7	4.9	4.5	4.2
Gypsum Saturation Feed, %	114.8	87.9	-	-	139.7
Gypsum Saturation Effluent, %	129.2	85.9	-	-	208.0
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	3.0	3.0	1.2	1.2	1.2
Flue Gas O_2, v%	9.9	10.5	8.8	9.0	9.4
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	F5-2	F5-3	F8-1	F8-2	F8-3
Test Duration, hours	11	21	42	12	9
Date	1/28/82	2/1/82	2/2/82	2/4/82	2/4/82
Cl Concentration, mg/l	49600.0	49600.0	80130.0	80500.0	80500.0
L/G, l/cu. M	8.0	8.0	8.0	5.7	10.4
Feed Solids Conc., w%	10.5	10.4	10.1	9.8	11.4
Scrubber Feed pH	6.2	6.0	5.5	5.6	5.5
Scrubber Effluent pH	4.8	5.0	4.4	4.4	4.4
SO_2 Inlet Conc., PPM	2443.0	2495.0	2483.0	2514.0	2474.0
SO_2 Removal Efficiency, %	74.7	79.0	66.3	50.0	79.6
SO_2 Make-per-pass, mM	7.8	8.1	7.0	7.3	6.4
Limestone Utilization, %	84.0	49.0	80.0	78.0	85.0
Filter Cake Solids Conc., w%	78.2	79.3	78.5	80.7	78.7
Solids Settling Rate, cm/min	5.1	4.3	4.3	4.4	4.0
Gypsum Saturation Feed, %	-	-	128.8	-	-
Gypsum Saturation Effluent, %	-	-	157.1	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	1.6	1.2	1.2	1.2	1.2
Flue Gas O_2, v%	9.7	9.2	9.0	9.2	9.2
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	F8-4	F18-1	F18-2	F18-3	F18-4
Test Duration, hours	11	72	14	25	8
Date	2/5/82	2/8/82	2/11/82	2/16/82	2/17/82
Cl Concentration, mg/l	80500.0	179700.0	180100.0	180000.0	180000.0
L/G, l/cu. M	13.1	8.0	7.9	8.0	8.0
Feed Solids Conc., w%	10.5	9.9	9.9	10.2	9.9
Scrubber Feed pH	6.0	5.2	5.5	5.6	5.4
Scrubber Effluent pH	4.7	4.1	4.6	4.8	4.7
SO_2 Inlet Conc., PPM	2416.0	2502.0	2467.0	471.0	512.0
SO_2 Removal Efficiency, %	84.2	34.5	66.0	76.2	80.7
SO_2 Make-per-pass, mM	5.3	3.7	7.0	1.6	1.8
Limestone Utilization, %	85.0	61.1	19.3	80.0	84.0
Filter Cake Solids Conc., w%	79.2	79.4	-	70.0	-
Solids Settling Rate, cm/min	3.8	0.9	1.6	0.6	0.6
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	1.2	1.8	1.5	-	-
Flue Gas O_2, v%	9.3	10.6	10.8	11.3	11.2
Height Packing, cm	53.3	53.3	53.3	53.3	53.3

Test Identification Number	F18-5	FL-1	FN-1	FN-2	FN-3
Test Duration, hours	16	10	39	22	42
Date	2/18/82	2/24/82	7/12/82	7/15/82	7/20/82
Cl Concentration, mg/l	180000.0	0.0	30000.0	70000.0	90000.0
L/G, l/cu. M	7.9	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	10.0	7.0	9.7	11.1	9.7
Scrubber Feed pH	5.6	2.8	5.9	5.8	5.8
Scrubber Effluent pH	4.7	2.8	5.0	4.9	4.9
SO_2 Inlet Conc., PPM	504.0	2457.0	2540.0	2606.0	2550.0
SO_2 Removal Efficiency, %	87.7	37.3	82.9	79.1	76.6
SO_2 Make-per-pass, mM	2.0	4.1	8.5	8.0	7.9
Limestone Utilization, %	51.4	92.3	83.3	80.0	79.0
Filter Cake Solids Conc., w%	-	84.0	82.5	80.5	82.1
Solids Settling Rate, cm/min	0.7	-	-	3.3	2.8
Gypsum Saturation Feed, %	-	-	115.6	-	112.7
Gypsum Saturation Effluent, %	-	-	116.4	-	116.2
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	-	-	-
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	10.7	10.4	4.6	3.8	4.4
Height Packing, cm	53.3	53.3	-	-	-

Test Identification Number	FN-4	F2-2	F4-1	FN-5	FN-6
Test Duration, hours	17	26	22	63	28
Date	7/22/82	8/10/82	8/12/82	8/30/82	9/2/82
Cl Concentration, mg/l	90000.0	20000.0	40000.0	110000.0	150000.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	9.8	11.3	10.9	9.8	10.1
Scrubber Feed pH	5.6	5.7	5.5	5.6	5.4
Scrubber Effluent pH	4.6	4.6	4.3	4.6	4.4
SO_2 Inlet Conc., PPM	2470.0	2590.0	2550.0	2485.0	2519.0
SO_2 Removal Efficiency, %	72.4	79.5	76.5	70.1	61.0
SO_2 Make-per-pass, mM	7.4	8.2	7.7	7.4	6.2
Limestone Utilization, %	80.3	80.0	79.2	81.0	80.0
Filter Cake Solids Conc., w%	82.1	78.3	76.5	81.2	79.5
Solids Settling Rate, cm/min	–	3.6	3.2	3.5	2.6
Gypsum Saturation Feed, %	–	–	112.4	95.2	–
Gypsum Saturation Effluent, %	–	–	147.4	116.1	–
DBA, Equiv. Adipic Acid mg/l	–	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	–	–	–	–	–
Flue Gas O_2, v%	4.2	5.4	5.4	6.5	3.0
Height Packing, cm	–	–	–	–	–

Test Identification Number	FB-1A	F5-1A	F8-1A	F10-1A	F16-1A
Test Duration, hours	48	42	62	74	78
Date	11/29/82	12/1/82	12/8/82	12/13/82	12/16/82
Cl Concentration, mg/l	0.0	50000.0	80000.0	100000.0	160000.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	9.6	10.1	10.3	10.1	10.2
Scrubber Feed pH	6.0	5.7	5.6	5.5	5.4
Scrubber Effluent pH	5.2	4.7	4.5	4.4	4.2
SO_2 Inlet Conc., PPM	2530.0	2560.0	2514.0	2560.0	2542.0
SO_2 Removal Efficiency, %	80.5	81.2	81.5	81.2	80.5
SO_2 Make-per-pass, mM	8.5	8.6	8.7	8.7	8.5
Limestone Utilization, %	84.0	85.0	85.0	85.0	84.0
Filter Cake Solids Conc., w%	77.3	81.2	77.4	81.2	79.3
Solids Settling Rate, cm/min	4.0	3.8	3.9	3.6	3.7
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	234.0	409.0	445.0	686.0
Ox. Air Stoich., Molar O_2/SO_2	1.3	1.3	1.3	1.3	1.3
Flue Gas O_2, v%	5.4	5.5	6.4	7.1	6.6
Height Packing, cm	-	-	-	-	-

Test Identification Number	FB-4	FB-5	F2-1A	F5-1B	F8-1B
Test Duration, hours	25	20	18	49	16
Date	1/6/83	1/11/83	1/13/83	1/17/83	1/20/83
Cl Concentration, mg/1	0.0	0.0	20000.0	50000.0	80000.0
L/G, 1/cu. M	8.3	8.3	7.8	8.3	8.3
Feed Solids Conc., w%	10.6	11.0	11.2	10.8	9.9
Scrubber Feed pH	5.2	5.1	5.2	4.9	4.8
Scrubber Effluent pH	3.0	3.7	3.9	3.8	3.7
SO_2 Inlet Conc., PPM	2421.0	2515.0	2402.0	2485.0	2456.0
SO_2 Removal Efficiency, %	50.2	90.9	90.3	91.6	90.5
SO_2 Make-per-pass, mM	4.9	9.3	10.1	9.5	9.3
Limestone Utilization, %	88.0	93.5	97.0	98.4	97.2
Filter Cake Solids Conc., w%	85.4	86.3	85.7	86.1	86.4
Solids Settling Rate, cm/min	4.3	4.0	4.1	4.3	3.9
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	750.0	750.0	825.0	950.0
Ox. Air Stoich., Molar O_2/SO_2	1.5	1.5	1.5	1.5	1.5
Flue Gas O_2, v%	5.1	4.7	5.3	5.1	5.1
Height Packing, cm	-	-	-	-	-

Test Identification Number	F12-1A
Test Duration, hours	69
Date	1/25/83
Cl Concentration, mg/l	120000.0
L/G, l/cu. M	8.3
Feed Solids Conc., w%	10.3
Scrubber Feed pH	4.5
Scrubber Effluent pH	3.6
SO_2 Inlet Conc., PPM	2454.0
SO_2 Removal Efficiency, %	87.1
SO_2 Make-per-pass, mM	9.0
Limestone Utilization, %	89.1
Filter Cake Solids Conc., w%	84.3
Solids Settling Rate, cm/min	3.6
Gypsum Saturation Feed, %	-
Gypsum Saturation Effluent, %	-
DBA, Equiv. Adipic Acid mg/l	1800.0
Ox. Air Stoich., Molar O_2/SO_2	2.0
Flue Gas O_2, v%	3.9
Height Packing, cm	-

Test Identification Number	MG-1	MG-2	MG-3	MG-4	MG-5
Test Duration, hours	75	65	94	96	38
Date	5/10/82	5/18/82	5/24/82	6/7/82	6/21/82
Cl Concentration, mg/l	0.0	5800.0	20000.0	50000.0	10000.0
L/G, l/cu. M	10.3	9.9	10.0	10.0	8.0
Feed Solids Conc., w%	9.8	9.8	9.8	9.6	100.0
Scrubber Feed pH	5.8	5.6	5.4	5.1	5.6
Scrubber Effluent pH	5.5	5.2	4.9	4.9	5.3
SO_2 Inlet Conc., PPM	2526.0	2512.0	2506.0	2487.0	2472.0
SO_2 Removal Efficiency, %	93.3	78.3	76.3	67.7	83.8
SO_2 Make-per-pass, mM	8.7	8.0	7.8	6.6	8.9
Limestone Utilization, %	85.0	81.9	81.0	82.3	83.3
Filter Cake Solids Conc., w%	55.7	66.7	67.1	66.3	70.6
Solids Settling Rate, cm/min	0.4	0.8	0.6	0.4	0.7
Gypsum Saturation Feed, %	-	-	134.6	-	29.5
Gypsum Saturation Effluent, %	-	-	206.2	-	33.8
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	10.7	9.0	9.6	7.1	5.4
Height Packing, cm	-	-	-	-	-

Test Identification Number	MG-6	MG-7	MG-8	MG-9	MG-10
Test Duration, hours	32	34	25	25	28
Date	6/28/82	7/6/82	7/7/82	7/28/82	8/2/82
Cl Concentration, mg/l	20000.0	40000.0	40000.0	70000.0	110000.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	9.6	10.1	10.1	11.2	10.1
Scrubber Feed pH	5.4	5.1	5.1	5.6	5.4
Scrubber Effluent pH	5.0	4.7	4.8	4.5	4.3
SO_2 Inlet Conc., PPM	2640.0	2478.0	2502.0	2465.0	2524.0
SO_2 Removal Efficiency, %	85.1	87.2	80.7	81.8	76.5
SO_2 Make-per-pass, mM	8.9	9.3	8.3	8.3	7.8
Limestone Utilization, %	83.1	83.0	81.0	80.4	79.8
Filter Cake Solids Conc., w%	62.7	70.6	65.4	80.4	79.8
Solids Settling Rate, cm/min	0.7	0.4	0.5	3.0	2.7
Gypsum Saturation Feed, %	36.1	10.9	25.9	16.1	-
Gypsum Saturation Effluent, %	44.4	12.2	26.5	17.8	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	-	-
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	5.4	5.0	4.9	8.6	8.7
Height Packing, cm	-	-	-	-	-

Test Identification Number	MG-11	MG-12	MG-13	MG-14	MG-15
Test Duration, hours	33	26	36	38	38
Date	8/4/82	9/8/82	9/14/82	9/15/82	9/21/82
Cl Concentration, mg/l	110000.0	80000.0	100000.0	140000.0	40000.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	10.6	9.9	10.2	9.7	10.1
Scrubber Feed pH	5.3	5.0	4.8	4.7	5.8
Scrubber Effluent pH	4.2	4.7	4.5	4.4	4.8
SO_2 Inlet Conc., PPM	2518.0	2506.0	2510.0	2530.0	2465.0
SO_2 Removal Efficiency, %	70.2	82.0	75.0	66.8	82.1
SO_2 Make-per-pass, mM	7.3	8.6	8.0	7.2	8.5
Limestone Utilization, %	79.4	84.0	82.0	81.0	79.0
Filter Cake Solids Conc., w%	79.4	56.8	57.1	56.3	81.5
Solids Settling Rate, cm/min	2.5	0.3	0.3	0.3	1.7
Gypsum Saturation Feed, %	6.6	3.7	-	0.2	-
Gypsum Saturation Effluent, %	6.7	4.1	-	0.2	-
DBA, Equiv. Adipic Acid mg/l	-	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	6.2	5.1	4.6	5.5	5.6
Height Packing, cm	-	-	-	-	-

Test Identification Number	MG-16
Test Duration, hours	37
Date	9/23/82
Cl Concentration, mg/l	150000.0
L/G, l/cu. M	8.0
Feed Solids Conc., w%	9.6
Scrubber Feed pH	5.4
Scrubber Effluent pH	4.3
SO_2 Inlet Conc., PPM	2468.0
SO_2 Removal Efficiency, %	67.7
SO_2 Make-per-pass, mM	6.9
Limestone Utilization, %	79.0
Filter Cake Solids Conc., w%	83.0
Solids Settling Rate, cm/min	1.4
Gypsum Saturation Feed, %	0.4
Gypsum Saturation Effluent, %	0.4
DBA, Equiv. Adipic Acid mg/l	0.0
Ox. Air Stoich., Molar O_2/SO_2	-
Flue Gas O_2, v%	5.7
Height Packing, cm	-

Test Identification Number	LB-1	L2-1	L4-1	L6-1	L8-1
Test Duration, hours	32	22	33	32	27
Date	10/4/82	10/6/82	10/11/82	10/13/82	10/18/82
Cl Concentration, mg/l	0.0	20000.0	40000.0	60000.0	80000.0
L/G, l/cu. M	8.0	8.0	8.0	8.0	8.0
Feed Solids Conc., w%	10.1	9.8	9.9	10.2	9.8
Scrubber Feed pH	5.7	5.7	5.8	5.6	5.6
Scrubber Effluent pH	4.7	3.8	3.7	3.3	3.2
SO_2 Inlet Conc., PPM	2550.0	2501.0	2465.0	2503.0	2437.0
SO_2 Removal Efficiency, %	80.1	77.1	65.7	63.7	54.8
SO_2 Make-per-pass, mM	8.2	7.8	7.0	6.6	5.6
Limestone Utilization, %	103.0	98.6	94.0	99.0	94.8
Filter Cake Solids Conc., w%	59.4	58.6	60.2	60.3	61.0
Solids Settling Rate, cm/min	0.4	0.4	0.4	0.4	0.3
Gypsum Saturation Feed, %	71.1	83.9	-	64.7	106.6
Gypsum Saturation Effluent, %	97.7	111.8	-	114.5	115.3
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	5.1	4.7	5.1	-	5.3
Height Packing, cm	-	-	-	-	-

Test Identification Number	L10-1	L7-1	L3-1	LB-2
Test Duration, hours	28	31	21	36
Date	10/25/82	10/27/82	11/1/82	11/3/82
Cl Concentration, mg/1	100000.0	70000.0	30000.0	0.0
L/G, 1/cu. M	4.4	4.4	4.4	4.4
Feed Solids Conc., w%	9.7	9.3	9.5	9.8
Scrubber Feed pH	5.7	5.7	5.8	5.7
Scrubber Effluent pH	3.7	3.7	4.0	5.1
SO_2 Inlet Conc., PPM	524.0	495.0	525.0	535.0
SO_2 Removal Efficiency, %	81.3	82.1	80.5	80.6
SO_2 Make-per-pass, mM	3.1	3.1	3.1	3.1
Limestone Utilization, %	98.3	99.3	99.2	97.5
Filter Cake Solids Conc., w%	62.4	62.4	63.7	62.7
Solids Settling Rate, cm/min	0.3	0.3	0.3	0.4
Gypsum Saturation Feed, %	-	117.4	-	75.3
Gypsum Saturation Effluent, %	-	127.8	-	85.2
DBA, Equiv. Adipic Acid mg/1	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-
Flue Gas O_2, v%	5.2	4.9	5.7	5.7
Height Packing, cm	-	-	-	-

Test Identification Number	CR-1A	CR-1B	CR-1C	CR-1D	CR-1E
Test Duration, hours	12	12	24	24	8
Date	1/31/83	2/1/83	2/2/83	2/3/83	2/4/83
Cl Concentration, mg/l	0.0	50000.0	50000.0	50000.0	50000.0
L/G, l/cu. M	8.3	8.3	8.4	8.4	8.3
Feed Solids Conc., w%	2.0	3.0	2.6	2.6	2.5
Scrubber Feed pH	5.8	5.1	5.0	5.0	5.0
Scrubber Effluent pH	5.3	4.4	4.4	4.5	4.5
SO_2 Inlet Conc., PPM	2442.0	2535.0	2434.0	2569.0	2211.0
SO_2 Removal Efficiency, %	79.1	68.3	69.1	68.0	67.7
SO_2 Make-per-pass, mM	8.7	7.5	7.6	7.5	7.2
Limestone Utilization, %	76.5	71.6	72.8	71.7	70.5
Filter Cake Solids Conc., w%	62.7	64.4	58.2	55.0	56.3
Solids Settling Rate, cm/min	1.1	0.7	0.5	0.4	0.4
Gypsum Saturation Feed, %	-	-	-	-	-
Gypsum Saturation Effluent, %	-	-	-	-	-
DBA, Equiv. Adipic Acid mg/l	0.0	0.0	0.0	0.0	0.0
Ox. Air Stoich., Molar O_2/SO_2	-	-	-	-	-
Flue Gas O_2, v%	5.0	6.7	6.4	6.8	6.9
Height Packing, cm	-	-	-	-	-

APPENDIX B

DATABASE TABLES OF AVERAGE LIQUID AND SOLID COMPOSITIONS

Test Identification Number	NB-1	N2-1	N3-1	N4-1	N4-3
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	385.0	10690.0	15600.0	22050.0	21800.0
Mg, mg/l	342.0	501.0	619.0	730.0	900.0
Na, mg/l	73.0	665.0	835.0	638.0	514.0
SO_3, mg/l	371.0	108.0	109.0	93.0	101.0
SO_4, mg/l	2106.0	881.0	826.0	900.0	674.0
CO_3, mg/l	542.0	270.0	277.0	288.0	266.0
Cl, mg/l	167.0	20560.0	31400.0	40530.0	40730.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	6.0	5.3	5.2	5.1	5.0
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	478.0	10870.0	16500.0	21830.0	21830.0
Mg, mg/l	330.0	513.0	618.0	729.0	923.0
Na, mg/l	81.0	700.0	832.0	650.0	529.0
SO_3, mg/l	786.0	318.0	296.0	263.0	351.0
SO_4, mg/l	2452.0	1289.0	1158.0	1322.0	735.0
CO_3, mg/l	322.0	218.0	251.0	187.0	202.0
Cl, mg/l	139.0	20200.0	31300.0	40720.0	40940.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.5	4.8	418.0	4.7	4.5
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	456.0	-	-	-	441.0
SO_2, mg/g	336.0	-	-	-	301.0
CO_2, mg/g	84.0	-	-	-	83.0
Ca, mg/g	283.0	-	-	-	294.0
Cl, Washed, mg/g	1.0	-	-	-	0.0
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	1.0	-	-	-	1.7
Mg, mg/g	2.0	-	-	-	1.7
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	481.0	-	-	-	437.0
SO_2, mg/g	336.0	-	-	-	297.0
CO_2, mg/g	70.0	-	-	-	78.0
Ca, mg/g	294.0	-	-	-	289.0
Cl, Washed, mg/g	1.0	-	-	-	7.0
Cl, Unwashed, mg/g	-	-	-	-	48.0
Na, mg/g	1.0	-	-	-	1.0
Mg, mg/g	1.8	-	-	-	1.8

Test Identification Number	N5-1	N10-1	NL-3	NN-1	NN-2
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	26600.0	53720.0	-	932.0	13850.0
Mg, mg/l	826.0	470.0	-	183.0	234.0
Na, mg/l	766.0	1080.0	-	16300.0	16650.0
SO_3, mg/l	183.0	28.0	-	428.0	194.0
SO_4, mg/l	829.0	458.0	-	2024.0	1183.0
CO_3, mg/l	205.0	205.0	-	541.0	237.0
Cl, mg/l	50100.0	101600.0	-	25700.0	50050.0
DBA, Equiv. Adipic mg/l	0.0	0.0	-	0.0	0.0
pH	4.9	4.6	-	5.9	5.2
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	26800.0	53970.0	-	1010.0	14050.0
Mg, mg/l	842.0	477.0	-	188.0	244.0
Na, mg/l	767.0	1132.0	-	16300.0	16550.0
SO_3, mg/l	370.0	96.0	-	949.0	421.0
SO_4, mg/l	999.0	655.0	-	2095.0	1607.0
CO_3, mg/l	120.0	164.0	-	327.0	149.0
Cl, mg/l	50100.0	102000.0	-	25400.0	50200.0
DBA, Equiv. Adipic mg/l	0.0	0.0	-	0.0	0.0
pH	4.5	4.0	-	5.5	4.8
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	461.0	432.0	-	-	-
SO_2, mg/g	300.0	223.0	-	-	-
CO_2, mg/g	88.0	76.3	-	-	-
Ca, mg/g	295.0	248.0	-	-	-
Cl, Washed, mg/g	0.0	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	1.0	1.0	-	-	-
Mg, mg/g	2.1	1.4	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	438.0	476.0	436.0	-	469.0
SO_2, mg/g	309.0	255.0	5.3	-	293.0
CO_2, mg/g	98.0	94.0	0.0	-	95.0
Ca, mg/g	303.0	309.0	240.0	-	299.0
Cl, Washed, mg/g	6.1	7.5	0.0	-	5.1
Cl, Unwashed, mg/g	39.0	52.3	0.0	-	0.0
Na, mg/g	1.0	1.0	1.0	-	1.7
Mg, mg/g	2.2	1.7	1.0	-	2.4

Test Identification Number	N1-1	NB-8	NB-9	NB-10	N5-LM1
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	5590.0	-	382.0	636.0	26770.0
Mg, mg/l	239.0	-	397.0	541.0	791.0
Na, mg/l	347.0	-	382.0	60.0	639.0
SO_3, mg/l	140.0	-	178.0	382.0	128.0
SO_4, mg/l	1332.0	-	294.0	3142.0	935.0
CO_3, mg/l	277.0	-	126.0	202.0	208.0
Cl, mg/l	10400.0	-	468.0	461.0	50800.0
DBA, Equiv. Adipic mg/l	0.0	-	0.0	-	-
pH	5.5	-	5.9	5.8	4.9
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	5560.0	-	388.0	720.0	26830.0
Mg, mg/l	230.0	-	386.0	563.0	818.0
Na, mg/l	333.0	-	387.0	65.0	673.0
SO_3, mg/l	472.0	-	307.0	865.0	322.0
SO_4, mg/l	1722.0	-	3208.0	3390.0	1394.0
CO_3, mg/l	88.0	-	68.0	128.0	128.0
Cl, mg/l	10300.0	-	448.0	473.0	50700.0
DBA, Equiv. Adipic mg/l	0.0	-	-	-	-
pH	4.9	-	5.5	5.4	4.4
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	465.0	523.0	-	576.0	610.0
SO_2, mg/g	347.0	350.0	-	389.0	342.0
CO_2, mg/g	88.0	52.4	-	38.0	40.0
Ca, mg/g	282.0	315.0	-	319.0	337.0
Cl, Washed, mg/g	7.9	-	-	-	5.3
Cl, Unwashed, mg/g	14.3	7.1	-	7.0	25.3
Na, mg/g	1.1	1.0	-	1.0	1.0
Mg, mg/g	1.7	1.5	-	1.4	1.7

Test Identification Number	N5-LM3	N5-HM1	N5-HM3	NS-1	NS-2
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	26600.0	26770.0	26700.0	1126.0	1315.0
Mg, mg/l	841.0	466.0	705.0	208.0	323.0
Na, mg/l	622.0	658.0	484.0	33.1	44.8
SO_3, mg/l	71.0	120.0	190.0	272.0	288.0
SO_4, mg/l	986.0	893.0	881.0	1531.0	1907.0
CO_3, mg/l	145.0	251.0	136.0	181.0	235.0
Cl, mg/l	50400.0	50530.0	50630.0	3283.0	1913.0
DBA, Equiv. Adipic mg/l	-	-	-	0.0	0.0
pH	5.4	5.0	5.1	5.7	5.7
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	26500.0	26670.0	26530.0	1315.0	1400.0
Mg, mg/l	862.0	467.0	727.0	214.0	322.0
Na, mg/l	625.0	655.0	483.0	32.2	40.0
SO_3, mg/l	116.0	290.0	111.0	747.0	644.0
SO_4, mg/l	1134.0	1366.0	1096.0	2480.0	2353.0
CO_3, mg/l	105.0	155.0	61.0	82.8	199.0
Cl, mg/l	50400.0	50500.0	50700.0	2533.0	1860.0
DBA, Equiv. Adipic mg/l	-	-	-	0.0	0.0
pH	5.1	4.5	4.7	5.2	5.4
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	-	510.0	530.0	437.0	434.0
SO_2, mg/g	-	357.0	343.0	256.0	254.0
CO_2, mg/g	-	37.0	47.8	116.0	106.0
Ca, mg/g	-	286.0	293.0	348.0	322.0
Cl, Washed, mg/g	-	7.0	5.7	-	-
Cl, Unwashed, mg/g	-	31.6	40.4	-	-
Na, mg/g	-	1.0	1.0	1.0	1.0
Mg, mg/g	-	1.1	1.5	138.0	1.4

Test Identification Number	NS-3	NS-4	NS-5	NN-3	N2-3
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	1158.0	25700.0	21600.0	1072.0	10670.0
Mg, mg/l	515.0	608.0	372.0	348.0	483.0
Na, mg/l	49.0	595.0	566.0	32600.0	568.0
SO_3, mg/l	249.0	66.2	127.0	389.0	122.0
SO_4, mg/l	2113.0	980.0	668.0	3304.0	708.0
CO_3, mg/l	228.0	159.0	189.0	349.0	300.0
Cl, mg/l	1853.0	52600.0	41800.0	50200.0	20030.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.9	4.9	4.6	5.9	5.2
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	1342.0	26200.0	21400.0	1106.0	10670.0
Mg, mg/l	533.0	626.0	382.0	355.0	493.0
Na, mg/l	51.4	622.0	600.0	32460.0	561.0
SO_3, mg/l	700.0	163.0	465.0	981.0	359.0
SO_4, mg/l	2757.0	1118.0	1308.0	3395.0	997.0
CO_3, mg/l	198.0	234.0	109.0	200.0	172.0
Cl, mg/l	1817.0	52600.0	41400.0	50240.0	20100.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.4	4.8	4.3	5.5	4.6
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	520.0	513.0	516.0	540.0	432.0
SO_2, mg/g	342.0	247.0	298.0	361.0	303.0
CO_2, mg/g	62.4	83.4	75.6	48.6	79.0
Ca, mg/g	307.0	286.0	284.0	292.0	284.0
Cl, Washed, mg/g	-	7.4	7.7	-	6.9
Cl, Unwashed, mg/g	-	31.4	36.2	-	46.9
Na, mg/g	4.0	1.0	1.0	1.0	1.0
Mg, mg/g	3.8	1.5	144.0	1.6	2.4

Test Identification Number	NN-5	NB-1A	N5-4A	NB-5A	N2-2A
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	3770.0	395.0	26700.0	1660.0	10700.0
Mg, mg/l	437.0	241.0	372.0	611.0	492.0
Na, mg/l	51030.0	123.0	891.0	57.0	428.0
SO_3, mg/l	262.0	363.0	163.0	970.0	266.0
SO_4, mg/l	1741.0	2214.0	839.0	1728.0	1212.0
CO_3, mg/l	221.0	567.0	278.0	395.0	350.0
Cl, mg/l	80170.0	321.0	50300.0	1640.0	20100.0
DBA, Equiv. Adipic mg/l	0.0	0.0	533.0	781.0	883.0
pH	5.6	6.0	5.0	5.2	5.1
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	3780.0	489.0	26400.0	1610.0	10900.0
Mg, mg/l	439.0	230.0	341.0	581.0	500.0
Na, mg/l	51070.0	127.0	921.0	56.0	422.0
SO_3, mg/l	838.0	806.0	567.0	1394.0	725.0
SO_4, mg/l	1907.0	2572.0	954.0	1827.0	1477.0
CO_3, mg/l	137.0	312.0	164.0	205.0	179.0
Cl, mg/l	80130.0	347.0	50100.0	1580.0	20500.0
DBA, Equiv. Adipic mg/l	0.0	0.0	540.0	781.0	883.0
pH	5.2	5.6	4.5	4.6	4.6
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	526.0	461.0	448.0	521.0	543.0
SO_2, mg/g	384.0	327.0	315.0	388.0	369.0
CO_2, mg/g	46.0	78.0	89.0	65.0	31.0
Ca, mg/g	321.0	314.0	309.0	302.0	293.0
Cl, Washed, mg/g	5.9	1.0	6.1	-	5.7
Cl, Unwashed, mg/g	-	1.0	18.0	-	23.1
Na, mg/g	1.0	1.0	1.0	1.0	1.0
Mg, mg/g	1.4	1.8	2.1	2.6	1.6

Test Identification Number	N5-5A	N8-2A	N5-6A	N3-3A
HOLD TANK LIQUOR ANALYSES				
Ca, mg/l	26900.0	41900.0	21300.0	10600.0
Mg, mg/l	655.0	874.0	771.0	497.0
Na, mg/l	738.0	1540.0	5730.0	6050.0
SO_3, mg/l	202.0	165.0	315.0	421.0
SO_4, mg/l	841.0	780.0	1050.0	1218.0
CO_3, mg/l	307.0	266.0	251.0	295.0
Cl, mg/l	50300.0	80400.0	51700.0	28600.0
DBA, Equiv. Adipic mg/l	1080.0	2131.0	1117.0	1124.0
pH	4.7	4.4	4.7	4.9
SCRUBBER EFFLUENT LIQUOR ANALYSES				
Ca, mg/l	26800.0	41100.0	21500.0	11000.0
Mg, mg/l	669.0	840.0	714.0	500.0
Na, mg/l	709.0	1450.0	6460.0	6260.0
SO_3, mg/l	521.0	694.0	833.0	1066.0
SO_4, mg/l	967.0	794.0	1340.0	1500.0
CO_3, mg/l	140.0	178.0	157.0	188.0
Cl, mg/l	50800.0	80900.0	53500.0	29900.0
DBA, Equiv. Adipic mg/l	1080.0	2131.0	1117.0	1124.0
pH	4.2	3.9	4.2	4.4
HOLD TANK SOLIDS ANALYSES				
S as SO_3, mg/g	-	-	-	-
SO_2, mg/g	-	-	-	-
CO_2, mg/g	-	-	-	-
Ca, mg/g	-	-	-	-
Cl, Washed, mg/g	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-
Na, mg/g	-	-	-	-
Mg, mg/g	-	-	-	-
FILTER CAKE SOLIDS ANALYSES				
S as SO_3, mg/g	539.0	517.0	531.0	541.0
SO_2, mg/g	349.0	385.0	390.0	359.0
CO_2, mg/g	32.5	52.0	17.4	32.0
Ca, mg/g	296.0	323.0	288.0	331.0
Cl, Washed, mg/g	10.1	7.5	-	5.6
Cl, Unwashed, mg/g	31.2	79.6	21.2	-
Na, mg/g	1.0	1.0	1.4	0.9
Mg, mg/g	1.6	1.4	1.3	1.1

Test Identification Number	FB-1	FB-2	F5-1	F8-1	F18-1
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	656.0	481.0	26930.0	43370.0	104300.0
Mg, mg/l	437.0	575.0	640.0	542.0	409.0
Na, mg/l	782.0	1002.0	603.0	1135.0	2790.0
SO_3, mg/l	1.0	10.0	3.4	9.0	1.8
SO_4, mg/l	4438.0	4938.0	964.0	671.0	0.0
CO_3, mg/l	183.0	121.0	7.4	68.0	1.8
Cl, mg/l	124.0	130.0	50200.0	80130.0	179700.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	6.6	7.1	5.7	5.5	5.2
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	756.0	500.0	26700.0	45500.0	102300.0
Mg, mg/l	449.0	555.0	652.0	470.0	391.0
Na, mg/l	811.0	970.0	610.0	1229.0	2683.0
SO_3, mg/l	485.0	133.0	389.0	374.0	66.0
SO_4, mg/l	4788.0	4969.0	1445.0	796.0	0.0
CO_3, mg/l	240.0	135.0	96.4	128.0	66.0
Cl, mg/l	125.0	129.0	49600.0	80500.0	180700.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.6	6.3	4.6	4.4	4.1
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	423.0	422.0	-	-	-
SO_2, mg/g	37.0	3.0	-	-	-
CO_2, mg/g	60.0	42.0	-	-	-
Ca, mg/g	257.0	264.0	-	-	-
Cl, Washed, mg/g	1.0	1.0	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	1.0	1.0	-	-	-
Mg, mg/g	1.5	1.3	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	446.0	426.0	489.0	493.0	381.0
SO_2, mg/g	42.0	19.0	7.5	13.5	4.2
CO_2, mg/g	51.0	41.0	35.2	66.0	172.0
Ca, mg/g	274.0	260.0	285.0	289.0	326.0
Cl, Washed, mg/g	1.0	1.0	16.4	9.7	19.5
Cl, Unwashed, mg/g	-	-	33.5	15.5	53.1
Na, mg/g	1.0	1.0	1.0	1.0	1.0
Mg, mg/g	1.6	1.3	1.8	1.4	3.7

Test Identification Number	F18-3	FN-1	FN-3	F4-1	FN-5
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	100000.0	2287.0	2436.0	22170.0	2460.0
Mg, mg/l	456.0	521.0	485.0	756.0	542.0
Na, mg/l	2527.0	20000.0	58400.0	646.0	72070.0
SO_3, mg/l	8.5	7.5	0.9	59.0	0.9
SO_4, mg/l	0.0	4542.0	4772.0	886.0	3883.0
CO_3, mg/l	128.0	62.0	25.0	86.0	26.0
Cl, mg/l	180000.0	32370.0	90000.0	40130.0	112000.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.6	5.9	5.8	5.5	5.6
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	100700.0	2340.0	2556.0	22100.0	1397.0
Mg, mg/l	459.0	523.0	499.0	751.0	474.0
Na, mg/l	2540.0	20070.0	58500.0	650.0	71270.0
SO_3, mg/l	32.7	449.0	445.0	280.0	414.0
SO_4, mg/l	0.0	4512.0	4826.0	1134.0	3673.0
CO_3, mg/l	145.0	127.0	98.0	154.0	76.0
Cl, mg/l	180000.0	32370.0	89870.0	40130.0	112700.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	4.8	5.0	4.9	4.3	3.6
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	455.0	471.0	466.0	486.0	379.0
SO_2, mg/g	3.3	0.0	0.0	135.0	0.0
CO_2, mg/g	110.0	66.0	76.0	55.0	50.3
Ca, mg/g	335.0	314.0	318.0	306.0	254.0
Cl, Washed, mg/g	11.4	8.4	4.8	4.6	-
Cl, Unwashed, mg/g	23.4	17.1	15.2	18.1	22.1
Na, mg/g	1.0	1.0	1.0	1.0	1.0
Mg, mg/g	1.7	1.3	1.2	1.7	1.6

Test Identification Number	F5-1A	F8-1A	F16-1A	FB-5	F8-1B
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	31200.0	42300.0	85700.0	1360.0	42600.0
Mg, mg/l	664.0	552.0	454.0	364.0	803.0
Na, mg/l	748.0	1510.0	2290.0	68.3	1211.0
SO_3, mg/l	0.0	0.0	0.0	0.0	0.0
SO_4, mg/l	832.0	680.0	399.0	1452.0	572.0
CO_3, mg/l	82.0	104.0	87.0	-	76.0
Cl, mg/l	48900.0	80900.0	161000.0	1450.0	79200.0
DBA, Equiv. Adipic mg/l	825.0	446.0	679.0	750.0	950.0
pH	4.9	5.6	5.4	5.1	4.8
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	31400.0	42600.0	85100.0	1400.0	41900.0
Mg, mg/l	698.0	526.0	478.0	391.0	811.0
Na, mg/l	744.0	1470.0	2310.0	57.1	1313.0
SO_3, mg/l	680.0	439.0	371.0	42.6	712.0
SO_4, mg/l	912.0	733.0	357.0	1488.0	633.0
CO_3, mg/l	162.0	42.0	31.0	-	-
Cl, mg/l	50270.0	80300.0	158000.0	1670.0	80300.0
DBA, Equiv. Adipic mg/l	825.0	438.0	687.0	750.0	950.0
pH	3.8	4.5	4.2	3.7	3.7
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	525.0	458.0	466.0	490.0	560.0
SO_2, mg/g	0.0	12.0	14.0	0.0	0.0
CO_2, mg/g	2.6	51.0	43.0	3.2	3.9
Ca, mg/g	263.0	315.0	317.0	248.0	282.0
Cl, Washed, mg/g	3.4	-	5.1	1.0	3.2
Cl, Unwashed, mg/g	8.9	14.0	17.0	1.0	13.3
Na, mg/g	1.0	1.0	1.0	1.0	1.0
Mg, mg/g	1.0	1.7	1.7	1.0	1.0

Test Identification Number	F12-1A
HOLD TANK LIQUOR ANALYSES	
Ca, mg/l	65100.0
Mg, mg/l	1040.0
Na, mg/l	2000.0
SO_3, mg/l	480.0
SO_4, mg/l	361.0
CO_3, mg/l	67.0
Cl, mg/l	121500.0
DBA, Equiv. Adipic mg/l	1800.0
pH	4.3
SCRUBBER EFFLUENT LIQUOR ANALYSES	
Ca, mg/l	67300.0
Mg, mg/l	934.0
Na, mg/l	1930.0
SO_3, mg/l	1073.0
SO_4, mg/l	470.0
CO_3, mg/l	115.0
Cl, mg/l	119000.0
DBA, Equiv. Adipic mg/l	1800.0
pH	3.4
HOLD TANK SOLIDS ANALYSES	
S as SO_3, mg/g	-
SO_2, mg/g	-
CO_2, mg/g	-
Ca, mg/g	-
Cl, Washed, mg/g	-
Cl, Unwashed, mg/g	-
Na, mg/g	-
Mg, mg/g	-
FILTER CAKE SOLIDS ANALYSES	
S as SO_3, mg/g	505.0
SO_2, mg/g	16.5
CO_2, mg/g	19.7
Ca, mg/g	277.0
Cl, Washed, mg/g	3.7
Cl, Unwashed, mg/g	16.9
Na, mg/g	1.0
Mg, mg/g	1.0

Test Identification Number	MG-1	MG-2	MG-3	MG-4	MG-5
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	580.0	2730.0	9656.0	23380.0	879.0
Mg, mg/l	1969.0	2030.0	1978.0	1970.0	4250.0
Na, mg/l	29.3	165.0	395.0	677.0	235.0
SO_3, mg/l	664.0	230.0	91.0	94.0	580.0
SO_4, mg/l	7312.0	1861.0	1729.0	-	3036.0
CO_3, mg/l	232.0	212.0	267.0	167.0	292.0
Cl, mg/l	1274.0	9568.0	22700.0	49500.0	10830.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.7	5.4	5.4	5.1	5.6
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	754.0	2794.0	9796.0	23260.0	865.0
Mg, mg/l	2054.0	2095.0	2034.0	1996.0	4300.0
Na, mg/l	29.5	160.0	405.0	690.0	224.0
SO_3, mg/l	1144.0	608.0	375.0	299.0	1280.0
SO_4, mg/l	8500.0	2732.0	2651.0	-	3604.0
CO_3, mg/l	157.0	126.0	151.0	122.0	184.0
Cl, mg/l	1271.0	9075.0	22040.0	49700.0	1103.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.4	5.1	4.9	4.9	5.3
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	586.0	526.0	548.0	541.0	510.0
SO_2, mg/g	372.0	343.0	387.0	374.0	383.0
CO_2, mg/g	41.8	46.1	41.0	39.6	42.0
Ca, mg/g	320.0	307.0	292.0	297.0	308.0
Cl, Washed, mg/g	-	-	4.4	-	1.7
Cl, Unwashed, mg/g	-	-	21.1	-	8.5
Na, mg/g	1.0	1.4	1.0	1.0	1.0
Mg, mg/g	1.0	1.4	1.2	1.5	1.6

Test Identification Number	MG-6	MG-7	MG-8	MG-9	MG-11
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	1328.0	1035.0	10800.0	3227.0	30970.0
Mg, mg/l	6963.0	14100.0	7010.0	23230.0	18200.0
Na, mg/l	255.0	328.0	590.0	1577.0	2213.0
SO_3, mg/l	940.0	1528.0	128.0	7.1	11.1
SO_4, mg/l	4194.0	4195.0	654.0	6883.0	846.0
CO_3, mg/l	349.0	333.0	254.0	44.3	39.5
Cl, mg/l	19580.0	40780.0	40430.0	70170.0	111700.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.4	5.1	5.1	5.6	5.6
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	1570.0	1032.0	10930.0	3263.0	31070.0
Mg, mg/l	6903.0	14130.0	7020.0	23330.0	18300.0
Na, mg/l	256.0	343.0	582.0	1560.0	2150.0
SO_3, mg/l	1813.0	2339.0	318.0	448.0	447.0
SO_4, mg/l	4370.0	4679.0	666.0	7178.0	882.0
CO_3, mg/l	209.0	153.0	195.0	99.2	99.0
Cl, mg/l	20350.0	40600.0	40430.0	70170.0	111700.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.0	4.7	4.8	4.5	4.6
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	559.0	558.0	-	440.0	440.0
SO_2, mg/g	416.0	390.0	-	1.9	5.8
CO_2, mg/g	53.0	38.0	-	59.0	54.6
Ca, mg/g	319.0	308.0	-	286.0	272.0
Cl, Washed, mg/g	1.7	6.1	-	3.8	7.8
Cl, Unwashed, mg/g	10.5	24.1	-	11.7	21.5
Na, mg/g	1.0	1.0	-	1.0	1.0
Mg, mg/g	1.7	2.4	-	1.2	18.0

Test Identification Number	MG-12	MG-14	MG-16
HOLD TANK LIQUOR ANALYSES			
Ca, mg/l	2177.0	1447.0	2327.0
Mg, mg/l	27870.0	47230.0	51330.0
Na, mg/l	1207.0	1117.0	1347.0
SO_3, mg/l	1105.0	1421.0	21.0
SO_4, mg/l	4090.0	3223.0	6790.0
CO_3, mg/l	303.0	304.0	120.0
Cl, mg/l	80530.0	140300.0	147300.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0
pH	5.0	4.7	5.4
SCRUBBER EFFLUENT LIQUOR ANALYSES			
Ca, mg/l	2183.0	1457.0	2330.0
Mg, mg/l	27900.0	47300.0	51400.0
Na, mg/l	1207.0	1117.0	1337.0
SO_3, mg/l	1663.0	1792.0	328.0
SO_4, mg/l	4441.0	3930.0	6990.0
CO_3, mg/l	170.0	213.0	85.0
Cl, mg/l	80700.0	140300.0	147300.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0
pH	4.7	4.4	4.3
HOLD TANK SOLIDS ANALYSES			
S as SO_3, mg/g	-	-	-
SO_2, mg/g	-	-	-
CO_2, mg/g	-	-	-
Ca, mg/g	-	-	-
Cl, Washed, mg/g	-	-	-
Cl, Unwashed, mg/g	-	-	-
Na, mg/g	-	-	-
Mg, mg/g	-	-	-
FILTER CAKE SOLIDS ANALYSES			
S as SO_3, mg/g	521.0	513.0	437.0
SO_2, mg/g	380.0	364.0	9.1
CO_2, mg/g	54.0	53.0	51.0
Ca, mg/g	320.0	306.0	275.0
Cl, Washed, mg/g	2.9	5.3	6.0
Cl, Unwashed, mg/g	15.1	48.0	27.0
Na, mg/g	1.0	1.0	1.0
Mg, mg/g	2.4	7.4	2.5

Test Identification Number	LB-1	L2-1	L6-1	L8-1	L7-1
HOLD TANK LIQUOR ANALYSES					
Ca, mg/l	716.0	11200.0	31870.0	44600.0	39000.0
Mg, mg/l	915.0	792.0	958.0	1060.0	917.0
Na, mg/l	82.0	425.0	937.0	1627.0	1590.0
SO_3, mg/l	414.0	25.0	51.0	0.0	21.0
SO_4, mg/l	2831.0	840.0	439.0	665.0	731.0
CO_3, mg/l	53.0	39.0	32.0	40.0	53.0
Cl, mg/l	1700.0	20170.0	60370.0	80670.0	70470.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	5.7	5.7	5.8	5.6	5.7
SCRUBBER EFFLUENT LIQUOR ANALYSES					
Ca, mg/l	905.0	11270.0	32530.0	44630.0	38970.0
Mg, mg/l	908.0	825.0	965.0	1077.0	941.0
Na, mg/l	86.0	405.0	947.0	1630.0	1593.0
SO_3, mg/l	1295.0	806.0	783.0	565.0	208.0
SO_4, mg/l	3316.0	1125.0	768.0	723.0	796.0
CO_3, mg/l	63.0	55.0	32.0	45.0	61.0
Cl, mg/l	1787.0	20000.0	60330.0	80500.0	70770.0
DBA, Equiv. Adipic mg/l	0.0	0.0	0.0	0.0	0.0
pH	4.7	3.8	3.3	3.2	3.7
HOLD TANK SOLIDS ANALYSES					
S as SO_3, mg/g	-	-	-	-	-
SO_2, mg/g	-	-	-	-	-
CO_2, mg/g	-	-	-	-	-
Ca, mg/g	-	-	-	-	-
Cl, Washed, mg/g	-	-	-	-	-
Cl, Unwashed, mg/g	-	-	-	-	-
Na, mg/g	-	-	-	-	-
Mg, mg/g	-	-	-	-	-
FILTER CAKE SOLIDS ANALYSES					
S as SO_3, mg/g	561.0	579.0	575.0	572.0	561.0
SO_2, mg/g	384.0	383.0	381.0	393.0	383.0
CO_2, mg/g	23.8	26.4	24.8	23.8	10.4
Ca, mg/g	314.0	318.0	314.0	317.0	312.0
Cl, Washed, mg/g	8.5	10.4	10.2	8.2	8.3
Cl, Unwashed, mg/g	9.5	30.5	38.3	60.2	61.0
Na, mg/g	1.0	1.0	1.0	1.0	1.0
Mg, mg/g	0.6	0.5	2.1	1.0	0.7

Test Identification Number	LB-2

HOLD TANK LIQUOR ANALYSES

Ca, mg/l	702.0
Mg, mg/l	40.0
Na, mg/l	25.0
SO_3, mg/l	432.0
SO_4, mg/l	1333.0
CO_3, mg/l	56.0
Cl, mg/l	250.0
DBA, Equiv. Adipic mg/l	0.0
pH	5.7

SCRUBBER EFFLUENT LIQUOR ANALYSES

Ca, mg/l	748.0
Mg, mg/l	40.0
Na, mg/l	27.0
SO_3, mg/l	669.0
SO_4, mg/l	1397.0
CO_3, mg/l	55.0
Cl, mg/l	245.0
DBA, Equiv. Adipic mg/l	0.0
pH	5.1

HOLD TANK SOLIDS ANALYSES

S as SO_3, mg/g	-
SO_2, mg/g	-
CO_2, mg/g	-
Ca, mg/g	-
Cl, Washed, mg/g	-
Cl, Unwashed, mg/g	-
Na, mg/g	-
Mg, mg/g	-

FILTER CAKE SOLIDS ANALYSES

S as SO_3, mg/g	545.0
SO_2, mg/g	397.0
CO_2, mg/g	16.2
Ca, mg/g	309.0
Cl, Washed, mg/g	7.1
Cl, Unwashed, mg/g	8.2
Na, mg/g	1.0
Mg, mg/g	1.0

Test Identification Number	CR-1C	CR-1E
HOLD TANK LIQUOR ANALYSES		
Ca, mg/1	26400.0	-
Mg, mg/1	243.0	-
Na, mg/1	870.0	-
SO_3, mg/1	176.0	-
SO_4, mg/1	1151.0	-
CO_3, mg/1	248.0	-
Cl, mg/1	50100.0	-
DBA, Equiv. Adipic mg/1	0.0	-
pH	5.0	-
SCRUBBER EFFLUENT LIQUOR ANALYSES		
Ca, mg/1	26400.0	-
Mg, mg/1	249.0	-
Na, mg/1	888.0	-
SO_3, mg/1	555.0	-
SO_4, mg/1	1386.0	-
CO_3, mg/1	174.0	-
Cl, mg/1	50400.0	-
DBA, Equiv. Adipic mg/1	0.0	-
pH	4.4	-
HOLD TANK SOLIDS ANALYSES		
S as SO_3, mg/g	-	-
SO_2, mg/g	-	-
CO_2, mg/g	-	-
Ca, mg/g	-	-
Cl, Washed, mg/g	-	-
Cl, Unwashed, mg/g	-	-
Na, mg/g	-	-
Mg, mg/g	-	-
FILTER CAKE SOLIDS ANALYSES		
S as SO_3, mg/g	-	529.0
SO_2, mg/g	-	307.0
CO_2, mg/g	-	84.2
Ca, mg/g	-	332.0
Cl, Washed, mg/g	-	5.6
Cl, Unwashed, mg/g	-	39.1
Na, mg/g	-	1.0
Mg, mg/g	-	1.2